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The Journal of the SOCIETY OF DYERS AND COLOURISTS

Volume 71 Number 2

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THE SOCIETY OF DYERS AND COLOURISTS
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The Journal of the Society of Dyers and Colourists

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NOTICE TO MEMBERS AND SUBSCRIBERS

Readers requiring *general information* regarding the Official Notices, List of Officers of the Society, etc. should consult pages 1–6 of the January 1955 and pages 262–266 of the July 1954 issues of the *Journal*, or write to *The General Secretary*, The Society of Dyers and Colourists, Dean House, 19 Piccadilly, Bradford 1, Yorkshire (*Telephone* Bradford 25138–9). *Editorial Communications* should be addressed to *The Editor*, at the same address.

Forthcoming Papers

The following papers have been accepted by the Publications Committee, and will appear in future issues of the *Journal*—

LECTURES

The Preparation, Use, and Evaluation of Metallic Pigments — *G. W. Wendon*

COMMUNICATIONS

The Influence of the Physical State of Dyes upon their Light Fastness — *G. Baxter, C. H. Giles, Miss M. N. McKee, and N. Macaulay*

The Polarography of Azo Dyes — *J. de O. Cabral and H. A. Turner*

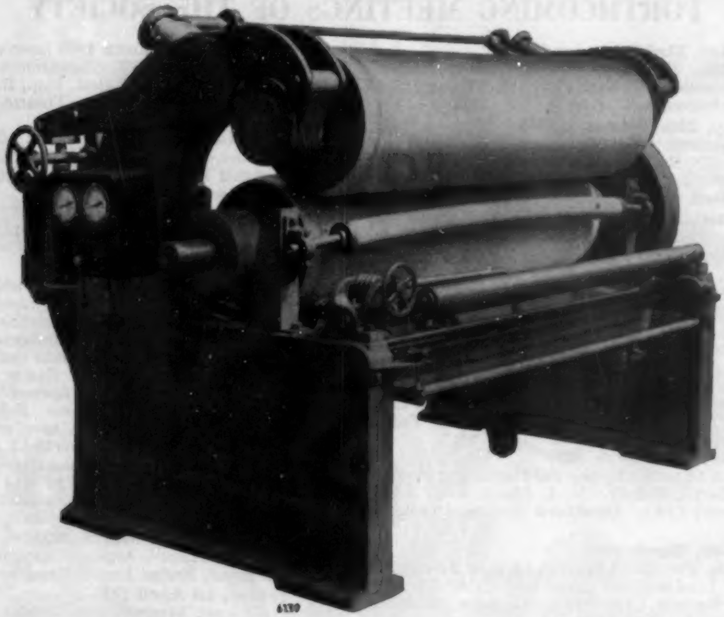
The Dyeing of Acetate Rayon with Disperse Dyes—
III—The Influence of Dispersing Agents on Rate of Dyeing — *Miss P. Harris, F. Manchester, and C. L. Bird*

The Effect on Wool of Boiling in Aqueous Solutions
II—Solutions of Ammonium Salts with and without Ammonia — *R. V. Peryman*

The Affinities of Vat Dyes in relation to their Constitution — *R. H. Peters and H. H. Sumner*

EXPLANATORY PAPERS ON MODERN THEORY

An Introduction to the Theory of Wool Dyeing
I—Equilibrium Theory of Affinity — *L. Peters*



FORTHCOMING MEETINGS OF THE SOCIETY

Wednesday, 23rd February 1955

MIDLANDS SECTION. *The Classification of Dyestuffs by their Dyeing Characteristics.* W. Beal, Esq., B.Sc. Kings Head Hotel, **Loughborough.** 7 p.m.

Thursday, 24th February 1955

WEST RIDING SECTION. *Heat Sensitivity of Anthraquinone Acid Wool Dyes.* Dr. R. H. Peters and Dr. T. Watson (Messrs. I.C.I. Ltd.). The Victoria Hotel, Bridge Street, **Bradford.** 7.30 p.m.

Friday, 25th February 1955

MANCHESTER SECTION. Annual Dance. Lesser Free Trade Hall, **Manchester.** 7.30 p.m.

Tuesday, 1st March 1955

LEEDS JUNIOR BRANCH. *The Application of Azoic Dyes to "Terylene" Polyester Fibre at 100-130° C.* H. R. Hadfield, Esq., M.Sc. (Messrs. I.C.I. Ltd.). Departmental Lecture Theatre, The University, **Leeds.** 3.30 p.m.

MANCHESTER JUNIOR BRANCH. *Synthetic Fibres in the Hosiery Industry.* Member of the staff of Clayton Dyestuffs Co., Manchester. (To be announced later). College of Technology, **Manchester.** 6.30 p.m.

Thursday, 3rd March 1955

BRADFORD JUNIOR BRANCH. *Dyeing and Finishing of Acetate Woven and Knitted Fabrics.* R. J. Mann, Esq., B.Sc. (British Celanese Ltd.). **Bradford** Technical College. 7.15 p.m.

Friday, 4th March 1955

LONDON SECTION. The Third London Lecture. *The Guilds of the City of London.* P. E. Jones, Esq. LL.B. (Deputy Keeper of the Records, Corporation of London). Waldorf Hotel, Aldwych, **London WC2.** 7 p.m.

MIDLANDS SECTION. MIDLANDS SECTION DINNER. Kings Head Hotel, **Loughborough.** 7 p.m.

Wednesday, 9th March 1955

NORTHERN IRELAND SECTION. Film Evening. (Joint Meeting with Textile Institute). Thompson's Restaurant, Donegall Place, **Belfast.** 7.30 p.m.

Thursday, 10th March 1955

MIDLANDS SECTION. *The Diffusion of Vat Dyes into Cellulose.* R. H. Peters, Esq., Ph.D., F.S.D.C., and T. Watson, Esq., Ph.D. (Dr. Peters lecturing). Gas Theatre, **Nottingham.** 7 p.m.

WEST RIDING SECTION. *What Dyeing does to Wool.* Dr. F. F. Elsworth (Wool Industries Research Association). The Victoria Hotel, Bridge Street, **Bradford.** 7.30 p.m.

Tuesday, 15th March 1955

HUDDERSFIELD SECTION. *Sulphur Colours for Special Purposes.* H. Senior, Esq. (James Robinson & Co. Ltd.). Preceded by Annual General Meeting, Princess Cafe, **Huddersfield.**

Tuesday, 15th March 1955 *(continued)*

LEEDS JUNIOR BRANCH. *The Classification of Dyes by their Dyeing Characteristics.* W. Beal, Esq., B.Sc. (The Geigy Co. Ltd.). Departmental Lecture Theatre, The University, **Leeds.** 3.30 p.m.

SCOTTISH SECTION — LADIES' EVENING. *The Hand Printing of Textiles.* E. S. Beton, Esq. (Brocklehurst, Whiston Amalgamated Ltd.). Institution of Engineers & Shipbuilders, **Glasgow.** 7 p.m.

Thursday, 17th March 1955

TWELFTH MERCER LECTURE, Midland Hotel, **Bradford.** 7.30 p.m. (See details below.)

Friday, 18th March 1955

MANCHESTER SECTION. One-day Symposium. *Laboratory Control of Dyeing and Finishing Processes.* Papers by— E. Atherton, Esq., B.Sc. *The Possibilities of Instrumental Control in Colour Matching.* S. Burgess, Esq., A.M.C.T., F.S.D.C. *The Use of Fastness Tables and Dyestuff Classification in the Formulation of Dyeing Recipes.* J. S. Ingham, Esq., B.Sc. *Colour-fastness. Correlation of Laboratory Tests with Customer Experience.* W. J. Marshall, Esq., B.Sc., A.R.I.C. *Control of Reducing Agent in Vat Dyebaths.* C. P. Tattersfield, Esq., F.T.I. *An Appreciation of the Value of Laboratory Tests for Textile Finishes.* The Symposium will be held in the Reynold's Hall, College of Technology, **Manchester,** commencing at 10.0 a.m. and finishing at 5.0 p.m.

Thursday, 24th March 1955

WEST RIDING SECTION—ANNUAL GENERAL MEETING. The Victoria Hotel, Bridge Street, **Bradford.** 7.30 p.m.

Friday, 1st April 1955

ANNUAL GENERAL MEETING AND DINNER of the Society. Queens Hotel, **Leeds.**

Tuesday, 5th April 1955

SCOTTISH SECTION — ANNUAL GENERAL MEETING. 7 p.m. *Primitive and Modern Dyeing Practice.* (Illustrated) (I.C.I. Ltd.). St. Enoch Hotel, **Glasgow.** 7.30 p.m.

Wednesday, 6th April 1955

MIDLANDS SECTION. Paper by G. H. Lister, Esq., B.Sc., Ph.D. (Subject later) (ANNUAL GENERAL MEETING at 6.30 p.m.). Kings Head Hotel, **Loughborough.**

Friday, 15th April 1955

MANCHESTER SECTION — ANNUAL GENERAL MEETING. *"Courpleta" The Dyeing and Other Properties of Triacetate Yarn and Staple.* J. Boulton, Esq., M.Sc. Tech., F.S.D.C., F.T.I. Textile Institute, **Manchester.** 7 p.m.

Thursday, 21st April 1955

MIDLANDS SECTION. *Some Experiences of a knitted-goods dyer.* A. W. Carpenter. (Joint Meeting with the Textile Institute Kidderminster Section). Carpet Trades Canteen. Mill Street, **Kidderminster.** 7 p.m.

THE SOCIETY OF DYERS AND COLOURISTS

Twelfth Mercer Lecture

The Twelfth Mercer Lecture will be given on Thursday 17th March 1955

at the

MIDLAND HOTEL BRADFORD at 7 30 pm

when the subject will be

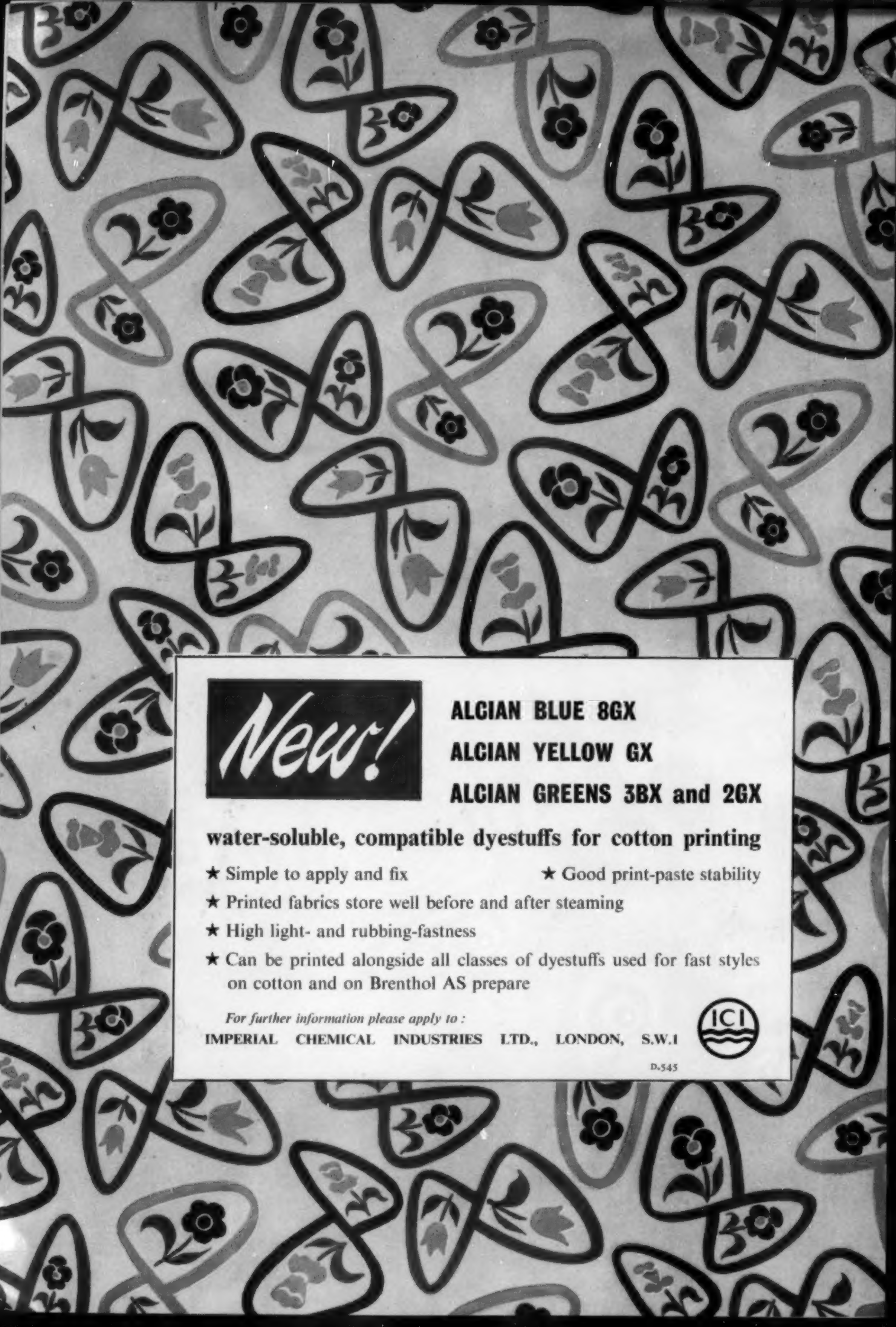
MODERN RESIN FINISHING

by

G. LANDELLS Esq B.Sc PH.D A.R.I.C F.S.D.C

The Deputy Chief Chemist (Research) Bradford Dyers Association Limited

The lecture is open to members of other societies and the public



THE JOURNAL
OF THE
Society of Dyers and Colourists

Volume 71 Number 2 FEBRUARY 1955 *Issued Monthly*

Proceedings of the Society

Examination for the Associateship (A.S.D.C.) held in November 1954

The first examinations for the Associateship of the Society of Dyers and Colourists were held in November 1954, and below appear the two sets of examination papers prepared for that occasion and the report of the Diplomas Executive Subcommittee on the examinations. It is hoped that publication of these papers and the report will be helpful to both prospective candidates and teachers, and that it will serve to inform members of the Society and others of the standard of knowledge expected from candidates for the Associateship.

Examination Papers

Papers A and B are taken by all candidates; but Papers C, D, and E are taken by a candidate only in his chosen branch of tinctorial technology. Further, in Paper E a candidate has a choice of subject—analytical and testing techniques or the organisation of production and economics

Paper A

General Chemistry and Properties of Dyes, Pigments, Auxiliary Products. General Chemistry and Properties of Organic High Polymers

10 a.m.–1 p.m. on 11 November 1954

(*SIX questions only to be attempted, three from each section of the paper*)

SECTION I

1. What chemical grouping characterises an azo dye? Indicate how this grouping may be introduced and give examples. Name and give the constitution of (*a*) an azo dye which dyes wool from an acid bath and (*b*) an azo dye which dyes cotton directly.

2. Phthalic anhydride is an important intermediate for making colouring matters. Name three dyes or pigments which are derived from it. Describe briefly, giving chemical equations where possible, the preparation and properties of one of them.

3. What type of chemical structure is necessary to enable a dye to form a complex with a metal? What metals (in the form of their salts) are generally employed and what advantages and disadvantages do the resulting dye–metal complexes possess? Give examples of such complexes applied to (*a*) cellulosic fibres and (*b*) protein and superpolyamide fibres.

4. Into what three main types may surface-active agents be classified? Give examples of each type and discuss in general terms the relationship between constitution and properties with particular reference to their application in the textile industry.

5. What is meant by a "disperse" dye? To what fibres may dyes of this type be applied? Outline the chemistry of this group of dyes with particular reference to the colour obtained and the fastness characteristics exhibited on the fibres to which they are normally applied.

6. Give an account of the chemistry of the formation of an insoluble azo dye. Outline methods of preparing stabilised diazo compounds for use in textile dyeing and printing.

7. Starting from anthraquinone, outline the essential stages in the production of (*a*) an acid dye, (*b*) a mordant dye, and (*c*) a vat dye based on this intermediate.

SECTION II

1. Explain the term *polyfunctionality*. Outline the essential features of (*a*) condensation polymerisation and (*b*) addition polymerisation.

2. Outline the chemistry of the processes involved in the production of (*a*) nylon and (*b*) phenol–formaldehyde resins.

3. Review critically the methods available for the determination of the molecular weights of high polymers.

4. High polymers can be broadly classified under the following three headings— highly elastic rubber-like materials, mouldable plastics, textile fibres. Discuss this classification from the point of view of their physical properties.

5. *Either* outline the constitution and properties of drying oils *or* discuss the mechanism of the vulcanisation of rubber.

6. Briefly discuss *either* the state of folding of the chain molecules in keratin and other polypeptides *or* the relative reactivities, in esterification and alkylation, of the hydroxyl groups in cellulose.

Paper B

Theories of Colour. Relation of Colour to Constitution. Colour Assessment and Colour Fastness

2–5 p.m. on 11 November 1954

(*SIX questions only to be attempted, including at least one question from each of the four sections of the paper*)

SECTION I

1. Describe how you would follow quantitatively the progress of dye absorption—

(*a*) of an acid levelling dye applied to wool from neutral solution in a long liquor

(*b*) of an acid milling dye applied to wool from an acid solution in a short liquor

(*c*) of a disperse dye by nylon.

Emphasise the differences in technique needed in the three cases.

2. Compare the relative merits and demerits of a photoelectric spectrophotometer and a photoelectric filter colorimeter for the estimation of dyes in solution.

3. Describe in detail, with diagrams, any piece of colour-measuring apparatus with which you are familiar and outline its uses in the study of dyeing.

4. Discuss the various uses of the word "dichroism" in connection with dyes and fibres.

SECTION II

5. Describe briefly, illustrating if necessary with diagrams, the meaning of *four* of the following terms—

(*a*) Chromaticity diagram

(*b*) Chroma

(*c*) Semichrome

(*d*) Uniform chromaticity

(*e*) Grey scale

(*f*) Purity

(*g*) Lightness.

6. Write a short essay on *one* of the following topics—

(*a*) Additive and subtractive colour mixing in relation to colour photography

(*b*) Artificial daylight lamps

(*c*) The testing of dyehouse operatives for defects in colour vision and colour aptitude.

7. Compare the relative merits of the Ostwald and Munsell systems of colour classification.

8. In establishing a new dyehouse, describe how you would arrange for the filing and cataloguing of colour matchings so as to be readily accessible for future reference.

SECTION III

9. Discuss the significance of "chromophores" and "auxochromes" in relation to the electronic theory of colour.

10. The dye benzeneazo-α-naphthol can exist in a number of tautomeric forms. Describe how the presence of these tautomers may be detected, and if possible how they may be isolated. Discuss their importance in connection with the colour of the compound.

11. Describe the absorption spectra of the triphenylmethane dyes, Crystal Violet and Malachite Green, and give the reasons why certain absorption bands have been identified with definite parts of the molecular structure.

12. Discuss the colour and constitution of substituted aminoanthraquinone vat dyes and the effect of hydrogen bonding to the carbonyl groupings.

SECTION IV

13. Three coloured fabrics, A, B and C, have the reflection spectra shown in tabular form below—

Wavelength (mμ.)	400	425	450	475	500	525	550	575	600	625	650	675	700
% Reflectance													
A	20	12	10	12	19	35	60	78	85	87	89	90	90
B	30	22	19	22	32	48	67	79	85	87	89	90	90
C	24	16	14	16	25	42	62	73	76	77	76	71	65

Draw the reflection curves on the graph paper provided and then answer the following questions—

(i) What is the colour of A?

(ii) Describe the colour difference between A and B and state how, assuming both to be dyeings on cloth, you would attempt to bring B to the same shade as A.

(iii) Describe the colour difference between A and C, and state whether C could be made to match A by the same method as used with B. If not, how could A and C be made to match?

14. Dyeings of a certain Dye A on wool over a range of concentrations gave the following colorimetric data—

	x	y	Lightness (%)
Undyed wool ...	0·343	0·330	80·5
0·06% Dye A ...	0·189	0·194	16·7
0·125% Dye A ...	0·175	0·149	11·0
0·25% Dye A ...	0·165	0·113	6·6
0·50% Dye A ...	0·168	0·093	4·4
1·00% Dye A ...	0·172	0·088	3·3
2·00% Dye A ...	0·183	0·082	2·6
4·00% Dye A ...	0·201	0·099	2·0
Faded Dyeing A...	0·170	0·141	10·1
Dye X	0·165	0·095	4·4
Faded Dye X ...	0·170	0·235	18·3

What colour is Dye A? Describe the changes of colour which take place as the depth of shade is increased. A 0·5% dyeing is exposed to light and after fading has the co-ordinates shown in the table. Describe the manner of fading and determine approximately the apparent depth of shade of the faded pattern. A matching to the 0·5% dyeing of A has the co-ordinates shown as Dye X in the table. After an equal light exposure its co-ordinates are as shown in the table. Describe the colour change during the fading of X and compare its light fastness qualitatively with that of A. (Graph paper may be used in answering this question.)

15. Solutions of Dyes A and B at a concentration of 1 g. per litre, and a mixture containing these dyes at unknown concentration, have the absorption spectra given in the table below. Determine the composition of the mixed solution, and state whether there is any evidence of interaction between the dyes.

Wavelength (mμ.)	425	450	475	500	525	550	575	600	625	650
Optical Density										
A	0·58	0·66	0·56	0·35	0·19	0·10	0·06	0·04	0·03	0·04
B	0·17	0·18	0·11	0·17	0·47	0·74	0·88	0·84	0·51	0·18
Mixture	0·61	0·67	0·51	0·47	0·82	1·17	1·36	1·28	0·79	0·29

BRANCH 1— TINCTORIAL TECHNOLOGY AS APPLIED TO TEXTILES

Paper C

Properties of Materials and Finished Products and Fundamental Mechanisms of the Industrial Processes

10 a.m.–1 p.m. on 12 November 1954

(*SIX questions only to be attempted*)

1. Give the structural formula for (*a*) part of a cellulose molecule, (*b*) the molecule of a typical direct cotton dye, and thence discuss recent speculations on the origin of the substantivity of this class of dyes for fibrous cellulose.

2. Describe investigations into the cause of tendering which occurs when some vat dyeings are exposed to light.

3. What is the function of soaping treatments normally applied to dyeings of certain fast ranges of dyes? Give a résumé of recent investigations and discussions on the subject.

4. Define the following physicochemical concepts— (*a*) Langmuir isotherm, (*b*) Gilbert–Rideal equation, (*c*) diffusion coefficient, (*d*) activity of a solute— and discuss the significance of any *one* of them in the fundamental study of dyeing processes.

5. Give an account of the water-soluble metal-sequestering agents available to the textile processer, dealing briefly with their chemistry, mode of action, and value in industrial dyeing processes.

6. Write brief notes upon *four* of the following with particular reference to their significance in textile printing— (*a*) *p*-hydroxydiphenyl, (*b*) retrogradation, (*c*) anomalous viscosity, (*d*) alkylcelluloses, (*e*) dimethylphenylbenzylammonium chloride, (*f*) thiodiethylene glycol.

7. Discuss the principles which underlie the production of resist effects in textile printing, giving illustrations from common commercial styles.

8. Write an appreciation of *one* of the following — (*a*) the Report of the Society's Committee on the Dyeing Properties of Wool Dyes, (*b*) the Reports of the Society's Fastness Tests Committee, (*c*) the Reports of the Society's Committee on the Dyeing Properties of Direct Cotton Dyes.

9. Draw a graph showing approximately the relative uptake, at equilibrium, of a level-dyeing acid dye by nylon, at different pH values from 8·0 to 0·5, with all other conditions constant. Interpret this graph in the light of recent investigations and speculations on the subject.

10. How are the co-ordinating properties of atoms of copper and other suitable metals utilised in dyeing procedures. Discuss the exploitation of these properties in (*a*) one traditional, (*b*) one recently devised process.

11. Define pH. How is the concept derived? Discuss the influence of the pH value of the dye liquor when dyeing wool with (*a*) acid dyes and (*b*) premetallised dyes.

12. Outline the dyeing characteristics of the following mixtures of fibres— (*a*) wool and cellulose acetate rayon, (*b*) wool and nylon.

13. Outline the difficulties which are being experienced in dyeing strongly hydrophobic fibres such as Terylene and Orlon, and indicate ways in which these are being overcome.

Paper D

Industrial Procedures and Plant

2–5 p.m. on 12 November 1954

(*SIX questions only to be attempted. The construction and operation of machines to be illustrated, where possible, with sketches*)

1. What are the essential features in the construction of (*a*) the winch dyeing machine, and (*b*) the jigger? What factors may influence the choice of one or the other of these for dyeing knitted or woven fabrics?

2. On what principles are the modern, continuous high-production systems for applying vat dyes based? Give details of *two* of these systems. What special advantages are claimed for each and how far are these claims justified?

3. Discuss critically the methods by which ladies' nylon hose may be prepared and dyed.

4. What are the essential parts of a modern multicolour roller printing machine and how do they work?

5. Describe typical package dyeing machines suitable for dyeing *one* of the following— (*a*) cotton yarn in cheeses, (*b*) wool tops, or (*c*) viscose rayon cakes. What special precautions are necessary when dyeing the kind of package selected,

with an appropriate dye, to obtain level, well penetrated dyeings, and to maintain the package in good form for subsequent use?

6. Why have many machines been recently designed to enable textiles to be dyed at above 100°C.? Describe such a machine. Are any special risks incurred when these systems are used?

7. Discuss the selection of dyes for and the method of applying them to fabrics consisting of (*a*) cotton and cellulose acetate rayon, (*b*) wool and viscose rayon, so as to produce in each case solid dyeings of good fastness to light and washing.

8. Describe the construction of pad mangles and discuss their use as dyeing machines.

9. How far is a "tensionless" jigger correctly named? When can it be used with advantage and how does one typical design work?

10. "The dyeing behaviour of textile materials is liable to be affected by preparatory treatments." Discuss this statement with reference to *three* of the following processes— (1) carbonising, (2) application of a shrink-resisting treatment, e.g. chlorination, to wool, (3) the bleaching of cotton, (4) high-temperature setting of nylon, and (5) the degumming of raw silk.

11. Write a brief essay on any *one* feature of dyeing or printing practice in which you are specially interested.

12. What are the functions of the steamer in textile printing? Illustrate your answer with examples chosen from among the practical methods for producing typical printing styles.

Paper E

10 a.m.–1 p.m. on 13 November 1954

(i) Analytical and Testing Techniques

(*FIVE questions only to be attempted*)

1. Describe two methods for determining the cause of damage to wool. Indicate the results to be expected from wool (i) undamaged, (ii) damaged by acid, (iii) damaged by alkali, (iv) damaged by light.

2. Describe the Congo Red test used for the detection of damage to cotton. Indicate the results to be expected from the various types of damage.

3. Describe tests for identifying the other fibre present in a blend of wool with *one* of the following — casein fibre, matt viscose, delustred acetate or nylon.

4. Describe in detail how you would analyse quantitatively any *two* of the following fibre mixtures— (i) viscose and mercerised cotton, (ii) pure silk and nylon, (iii) wool, viscose, and cotton.

5. Describe a method for determining the percentage of synthetic anionic detergent in a commercial product. Indicate the order of accuracy to be expected.

6. Discuss the use of chromatographic methods in the analysis of commercial dye mixtures.

7. Describe how you would differentiate between brown dyeings produced by azoic, vat, sulphur, and diazotised and developed direct cotton dyes on cotton.

8. Describe the principal methods of determining the percentage of residual acid in dyed wool. Indicate the method you prefer and give reasons for your choice.

9. Describe the tests you would use to differentiate between "baked" finishes on viscose rayon, produced by use of (i) acidified formaldehyde, (ii) urea–formaldehyde resin, (iii) melamine–formaldehyde resin. Describe the quantitative estimation of (*a*) total resin, and (*b*) free formaldehyde present in material that has been given a urea–formaldehyde resin finish.

10. Describe briefly the microchemical method you would use to determine the presence or absence of iron, copper, lead, or chromium compounds.

11. Material dyed in a circulating machine has a fine deposit on the surfaces of the packages which could be due to (i) peaty humus, (ii) iron rust, (iii) broken-down zeolite and/or sand or earthy matter. Describe how you would analyse the material to determine the nature of the deposit.

12. Write down fastness specifications (limited to three agencies) which you think would be suitable for the following fabrics— (i) viscose–acetate linings for women's suits, (ii) woollen cloth (piece-dyed) for women's outerwear, (iii) furnishing fabrics for domestic furniture, (iv) rayon blouse fabric. Describe in detail the methods of test you would use in checking the performance of bulk deliveries for *one* of the specifications only.

13. Discuss the development of the methods used for testing fastness to perspiration. Describe two commonly accepted methods and discuss their efficiency.

14. A viscose face, cotton back sateen is fast dyed in various colours, and after being in stock for a year is made up into bathing costumes. A number of complaints are received of the poor wearing qualities of the black costumes only, which easily fray and abrade. Describe the steps you would take to determine the cause of this fault.

15. A dye merchant sells a certain dye by description only (no sample being submitted) as 150% concentration. His customer rejects the delivery on the grounds that it is only 100% concentration compared with the standard 100% product of a well known maker. Give your opinion on the merits of the dispute and explain what is meant by a dye being declared as 100% concentration. How would you determine the strength of a batch of dye delivered to you?

16. Discuss the influence of the viscosity of printing pastes on the resultant print and describe the control methods which could be used in routine works practice.

(ii) Organisation of Production and Economics

(*FOUR questions only to be attempted*)

1. What points should be considered when investigating sites for a new dyeing or printing works? Give the order of importance of the various points and the reasons for their inclusion.

2. In deciding what dye to use a balance has to be struck between technical and economic considerations. Discuss this statement.

3. Describe the allocation of duties in a dyeing or printing firm.

4. Describe an ideal layout of plant for a particular branch of dyeing or printing. Give your reasons for your arrangement.

5. Textiles may be dyed as loose fibres, slubbing, yarn, pieces, or garments. Discuss the economic and technical considerations which influence both the dyeing method and the stage at which dyeing is carried out.

6. Describe a method for ascertaining the total costs of dyeing a batch of goods.

7. Discuss the function of a merchant converter.

8. Give an account of the control of the progress of work through a dyeing or printing works.

9. What are the relative functions of (*a*) the dyemakers' laboratories, (*b*) the Research Associations, and (*c*) a dyeing or printing firm's own staff, in the maintenance and improvement of quality?

10. How would you set about choosing a new machine for dyeing or printing a material of your own selection?

BRANCH 9—PRODUCTION OF DYES, LAKES, AND PIGMENTS

Paper C

Properties of Materials and Finished Products and Fundamental Mechanisms of the Industrial Processes

Three hours allowed

(*FOUR questions only to be attempted*)

1. Outline the necessary conditions under which ammonia will replace atoms or groups in (*a*) the benzene series, (*b*) the naphthalene series, (*c*) the anthraquinone series, to give primary amino compounds.

2. Discuss in detail methods of achieving diazotisation of primary aromatic amines, with illustrative examples.

3. Write a systematic account of the triphenylmethane series of dyes.

4. Give an account of the various types of water-soluble azo compounds which exhibit substantivity for cellulosic fibres.

5. How is β-aminoanthraquinone converted into vat dyes? Demonstrate how the structural formula of one of the vat dyes derived from it has been determined.

6. What methods are used for the preparation of solubilised forms of vat dyes of (*a*) the indigo and thioindigo series, and (*b*) the anthraquinone and related series?

7. How is quinizarin (1:4-dihydroxyanthraquinone) prepared? Describe how it may be converted into disperse dyes for cellulose acetate and into acid dyes for wool.

8. Give an account of the various types of molecular structure which enable a dye to give a complex with metals such as chromium.

9. Write a brief essay on the various methods of making iron oxide pigments, paying particular attention to the factors that influence the colour of the finished pigments.

10. Give an account of the properties of Prussian Blue and compare them with those of copper phthalocyanine.

11. Describe two methods of making pigments from basic dyes and compare the properties of the products.

Paper D

Industrial Procedures and Plant

Three hours allowed

(*FOUR questions only to be attempted*)

1. Describe in detail, giving particulars of the materials used for its construction, a plant for the manufacture of an insoluble azo pigment up to the stage of wet filter-press cake.

2. Explain with the aid of a diagram unidirectional back washing in a filter press. Make a list, suitable for the guidance of a new operative, of the essential points that must be observed when using a filter press.

3. Survey the usefulness of wood as a constructional material in the dye, lake, or pigment factory, pointing out its advantages and disadvantages over other materials. Name the varieties of timber most used in these types of factory.

4. What are the various types of equipment used for drying dyes, lakes, and pigments? Mention a typical application in each case. Describe one of these pieces of equipment in detail.

5. It is required to sulphonate a substance by adding to a solution of it in concentrated sulphuric acid, 60% oleum, heating at 130–140°c., cooling, diluting to an acid strength of 90% H_2SO_4, and then filtering so as to retain both the solid and the filtrate. Describe the plant you would use for the purpose.

6. Write an essay on *one* of the following—

(*a*) The application of plastics materials in the colour factory.

(*b*) "Blowing" *versus* "pumping" in dye and intermediate manufacture.

7. Give an account of the methods of grinding solid material to a powder, which find application in lake and pigment making. Describe a piece of

equipment capable of producing a powder the particle size of which is less than 5 μ.

8. A slurry, the aqueous phase of which consists of 15% H_2SO_4, is to be pumped from a tank into a filter press requiring an eventual pressure of 40–50 lb./sq.in. Give detailed information about the type of pipeline, valves, pump and filter fabric which would be best suited to this operation.

Paper E

Three hours allowed

(i) Analytical and Testing Techniques

(*FOUR questions only to be attempted*)

1. Given a water-insoluble powder, said to be a dye for application to textiles, describe how you would ascertain to what dyeing class, and to what chemical class of substance, it belongs.

2. Give details of methods of quantitative estimation of two of the following—

(*a*) 2:3-Hydroxynaphthoic acid

(*b*) Sulphanilic acid

(*c*) *p*-Nitroaniline

(*d*) H acid (1:8-aminonaphthol-3:6-disulphonic acid).

Discuss factors in the methods described which limit the accuracy of the results.

3. Write an account of the use of titanous salts as reagents in the quantitative estimation of dyes.

4. Given commercial samples in paste form of—

(*a*) a vat dye,

(*b*) a disperse dye,

describe methods for determining (i) the water content and (ii) the percentage of pure dye present.

5. Give an account of methods available for demonstrating that a given commercial water-soluble dye is a mixture. Describe methods of separating the constituent dyes of such a mixture.

6. An azoic printing composition consisting of a diazo compound in a stabilised form mixed with a coupling component is submitted for examination. Describe how you would propose to identify the diazo component and the coupling component present.

7. Give an account of the tests you would make to determine the suitability of a batch of zinc oxide for use in (*a*) rubber manufacture, (*b*) paints, (*c*) cosmetics.

8. How would you determine the covering power of (*a*) an organic pigment, (*b*) metal flake?

(ii) Organisation of Production and Economics

(*FOUR questions only to be attempted*)

1. Outline the duties and responsibilites of the Works Foreman in a dye- or pigment-making works.

2. Describe a method of costing the products of a colour works, with which you are familiar. Demonstrate why yield is the most important factor in keeping down individual manufacturing costs.

3. List the requirements in order of importance of an ideal site for a colour-making factory, giving reasons for including them.

4. What are the advantages and the disadvantages of bulk-storing liquids when compared with using them from drums, carboys, etc.? What special difficulties arise when corrosive liquids are used from bulk storage, and what provisions must be made to meet them?

5. Systematic preventive maintenance is regarded as the ideal way of keeping chemical plant in running order. Discuss this. Why is it usually regarded as the best system and why does its practical application sometimes give rise to difficulty?

6. Write a short essay on *one* of the following—

(*a*) Work study

(*b*) Safety in the colour works

(*c*) Welfare and the chemical worker.

7. Write an essay on the development of the colour-making industry in this country since Perkin's discovery of Mauve in 1856.

8. Discuss the value of pilot-scale work in the development of a process from the laboratory to the works. Describe in detail a piece of pilot plant of which you have had experience.

Report of the Diplomas Executive Subcommittee on the 1954 Associateship Examinations

At an early stage forty candidates intimated their intention of taking the examination, and arrangements were made for the examination to be held simultaneously in Bradford, Galashiels, and Cairo. However, before the examination was held many candidates asked for their application to be deferred until 1955, and finally only nine candidates sat for the examination— eight in Bradford and one in Galashiels. One candidate was taken ill during the examination, and so only eight candidates completed the examination.

The examination papers were designed to test not only the candidates' theoretical and practical knowledge but also their ability to apply that knowledge. The examiners found the task of setting the papers to be not at all easy, mainly because they did not know what background to assume for the candidates and because of the lack of any set courses designed to prepare the candidates for the theoretical portion of the examination. This difficulty was overcome to some extent by giving each examiner a list of the branches of

industry from which the candidates came. These were as follows—

(i) Garment dyeing
(ii) Dye merchanting
(iii) Teaching
(iv) Fabric printing
(v) Cotton and rayon piece dyeing.

Papers were prepared for two branches of tinctorial technology—

(1) Textiles
(2) Production of Dyes, Lakes, and Pigments

but ultimately only candidates taking the former presented themselves for examination.

Of the eight candidates who completed the examination, four passed; two satisfied the examiners in papers C, D, and E, but one of them was a borderline case in papers A and B, while the other failed them; and the remaining two candidates failed the examination as a whole.

The following are summaries of the examiners' comments on the candidates' written papers.

Paper A

Section I— General Chemistry and Properties of Dyes, etc.

The questions on the whole were answered satisfactorily, and most candidates showed adequate grasp of the subject.

Section II— General Chemistry and Properties of High Polymers

Most candidates seemed either not to be adequately prepared or not to have appreciated the standard required. Answers were very often sketchy, and in some cases the requirements of the question were not properly appreciated. It should be understood that mere tabulation of methods or features is not discussion of a topic. It was not generally realised that the paper dealt with high polymer chemistry generally and not solely with polymers of mainly textile interest. Future candidates should realise that details of production and properties of fibres, unless particularly requested, are irrelevent and no substitute for more fundamental knowledge.

Paper B

Theories of Colour, etc.

The quality of replies was low, in some cases extremely low, especially in Sections III and IV. On the whole candidates betrayed lack of practical experience, and half of them showed a most inadequate grasp of the subject. Preparation had obviously been unsatisfactory.

Paper C

Properties of the Materials and Finished Products and Fundamental Mechanisms of Industrial Processes in Tinctorial Technology as Applied to Textiles

Because of the relative unfamiliarity of the examination, wide choice of questions was given, and, to make up for scarcity of organised preparation, it was hoped to bring in some familiarity by including some subjects dealt with in the *Journal* in recent years.

The response was not quite as good as had been hoped for, but, in the special circumstances, was better than might have been expected. Even the weaker candidates wrote reasonably intelligently on the whole, but preparation had been insufficient, and many answers were superficial and lacked proper detail and precision. There was a tendency to evade questions which were primarily theoretical. In some subjects, e.g. effects of soaping (Question 3) or metal-sequestering agents (Question 5), replies were often thin and old fashioned, although these subjects have been covered in fairly recent issues of the *Journal*. That the level was not above the heads of candidates was shown by at least two very good sets of answers being given, the level and the consistency being very encouraging. On the whole the English and the spelling were much better than are sometimes encountered even in examinations at this level.

Paper D

Industrial Procedures and Plant Employed in Tinctorial Technology as Applied to Textiles

All candidates dealt with the questions in a sensible manner, explained themselves reasonably clearly and concisely, and showed adequate grasp of the subject. Future candidates should take particular care that, in answering a question concerning a machine or a process, they mention or refer to (however briefly) every feature which is of significance. There were signs that some of the candidates knew more about the machine or process than they actually mentioned.

Paper E

Here candidates had a choice of paper.

(i) Analytical and Testing Techniques Used in Tinctorial Technology as Applied to Textiles

Seven candidates took this paper. With one exception all candidates revealed good knowledge of the subject, one giving a remarkably good set of answers, while another was very good.

(ii) Organisation of Production and Economics in Tinctorial Technology as Applied to Textiles

One candidate took this paper. No course of tuition in this subject is available, there is no text-book dealing with it, and such scanty literature as exists is widely scattered. The candidate who took this paper was therefore faced with a set of questions whose like he could never have met before, and to answer which depended more on his ability to reason from facts gained in his everyday work than on any preparation for an examination. He therefore showed initiative and confidence in

himself even to attempt the paper, and in answering it he showed himself to be a careful and thoughtful observer well able to use accumulated knowledge and experience to deal with novel problems set before him. He dealt satisfactorily with the questions he attempted, but, as was to be expected, he betrayed obvious signs of the lack of any organised preparation for being faced with such questions.

INTERVIEW

Subsequent to the examination, all the candidates were interviewed by the Diplomas Executive Subcommittee. The recommendations of the Subcommittee regarding candidates form the subject of a separate report (see p. 104).

C. O. CLARK

Convener, Diplomas Executive Subcommittee

The Behaviour of Leuco Vat Dyes above 100°C.

S. BLACKBURN AND M. R. FOX

Meeting of the Manchester Section held at the Textile Institute, Manchester, on 15th January 1954, Mr. G. S. J. White in the chair

This preliminary study of the behaviour of vat dyes at high temperatures has included examination of the stability of these colouring matters, and some consideration has been given to the use of leuco-dye protective agents. A number of dyes stable at high temperatures are available, but known leuco-dye protective agents hold out little hope of extending the range to any great extent for the recently introduced package-dyeing systems. Examination of the behaviour of vat dyes over a wide range of temperatures and of their rate-of-dyeing curves has led to the development of a cooling bath process for the dyeing of cellulosic yarn packages. Improved migration, penetration, and level-dyeing behaviour are features of high-temperature dyeing; dyeing times may be shortened, and the process should prove to be attractive for dyeing tightly twisted mercerised cotton yarns and similar textiles.

Introduction

The availability of numerous package-dyeing and piece-dyeing machines capable of use at high temperatures has created a demand for an extension of our knowledge of the behaviour of dyes at temperatures higher than 100°C. A number of high-temperature dyeing machines are now in commercial operation, and the volume of scientific and technical press information on this subject has grown rapidly since 1948[1–9].

The experimental work upon which this paper has been based was confined to vat dyes on natural cellulosic yarns, but the broader picture of vat dye application to textile piece goods and fibres of regenerated cellulose, as well as of the hydrophobic synthetic fibres, must not be lost sight of. It is hoped that much of the information gained in this preliminary study will be of value to workers in these various fields.

Experimental

APPARATUS AND PROCEDURES USED

Preliminary tests, and many of the later small-scale experiments, were carried out in a canteen-type pressure cooker of 2 gal. (9 litres) capacity. The cooker was fitted with a combined temperature–pressure gauge and contained a metal grid platform supported some 2 in. from the base of the vessel. Eight porcelain dyepots of 250 ml. capacity could be used simultaneously, and comparative tests could be made in one operation. Dye stability tests and the trials with dye-damage inhibitors were carried out in this apparatus, but, since it was realised that liquor circulation and rate of flow of dye liquors play a vital part in the production of level dyeings, all work on dyeing rates, migration, etc. was carried out in a laboratory-scale Longclose high-temperature dyeing machine described later.

The general procedure in the pressure cooker trials was to dye 5-g. hanks of 2/20s bleached cotton yarn at a liquor : yarn ratio of 30 : 1. Dyebaths were prepared at 85–90°C., the yarn was entered, and the pressure vessel was closed. Direct heat was applied to the cooker, and temperatures of 110–130°C. were reached within 4 min. Dyeing was continued at high temperature for up to 40 min., and at the end of this period the vessel was cooled rapidly to 90°C. (4–5 min.) and the hanks were withdrawn for oxidation, souring, and soaping under orthodox conditions. The resultant dyeings were examined for hue, depth, and fastness properties alongside dyeings of equal depth prepared under normal application conditions on identical yarn.

In the tests for dye stability the partly exhausted dyebaths, after removal of the dyed yarn, were cooled to the temperature normally recommended for orthodox application, checked for bath condition, and adjusted by additions of caustic soda and/or hydrosulphite where necessary. Additions of salt (5 g./litre) were made to all the baths in order to ensure complete exhaustion on to cotton. The "exhaust" dyeings produced in this manner were critically examined for depth, hue, and fastness in order to check whether the dye remaining from the high-temperature bath had decomposed in any way.

The large-scale dyeing trials were made on cheeses in a Longclose laboratory stainless-steel high-temperature dyeing machine; a simplified diagram is shown in Fig. 1.

The machine consists of a large expansion tank A fitted with a lid which is secured by locking screws. Tank A carries a liquor level gauge and a baffle plate below which heating and cooling coils

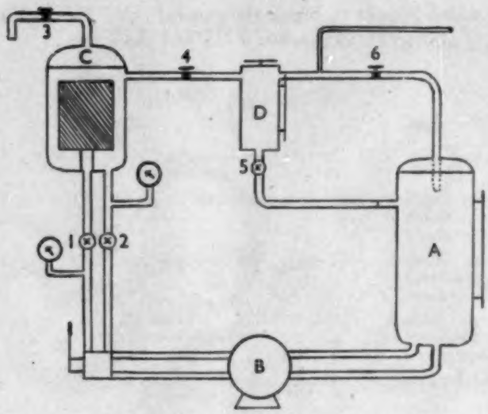


FIG. 1

are located. This tank is connected to a special centrifugal pump *B*, and through a two-way flow mechanism to the dyeing chamber *C*, which is capable of holding 1 or 2 cheeses of 1 lb. weight, giving liquor : goods ratios of 30 : 1 and 15 : 1 respectively. Provision is also made for cops, cones, and loose fibres. Pressure gauges are fitted close by the valves *1* and *2* below the dyeing chamber. The lid of *C* carries a safety valve and a let-off for entrapped air at valve *3* when dyeing is started.

Situated between and connected to *A* and *C* is an addition pot *D* of approx. 600 c.c. capacity, which can be completely isolated from the system by closing valves *4–6*. Additions can therefore be made at *D* without affecting the pressure or the temperature of the liquor in the main circuit. Temperature is automatically controlled.

Nitrogen supplied from a cylinder may be introduced along the narrow tube entering near *D* and is directed into *A*. By this means static pressures of 20–25 lb./sq. in. above atmospheric have been developed at 120°c.

The preferred dyeing process developed during the course of this work follows the general outline below and is given at this stage in order to describe the modus operandi. Water is circulated through the previously scoured package until a temperature of 90°c. is reached. A small amount of nitrogen is introduced to raise the gauge pressure to 5 lb. per sq.in. above that provided by the pump. Caustic soda and sodium hydrosulphite are then added to sharpen the bath, and circulation is continued while the temperature is raised to 120°c. This period requires approx. 15 min. from 90° to 120°c., and yields a pressure of 20–25 lb./sq.in.

The whole of the dye required for the experiment is reduced in a concentrated vat in a separate vessel and added via the addition pot to the main system. Dyeing commences immediately with circulation from the outside to the inside of the package, a reversal of flow occurring every 7 min. After 15 min. at 120°c. the steam is cut off and the cooling coils are set in operation, so that the dyebath is brought steadily and uniformly to the normal dyeing temperature for the dyes in use. If salt additions are required they are made by means of a drip feed during the cooling process, which is regulated to take 25–30 min. After 5 min. at this temperature, the dyebath is run off, and the dyeings are rinsed, oxidised, soured, and soaped with Lissapol NC in the conventional manner.

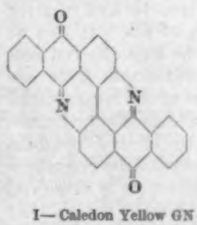
The rate-of-dyeing curves produced for this paper (Fig. 4 and 5) were based on optical measurement of samples of dye liquor drawn from the system at suitable intervals during the dyeing operation. The data for the temperature curves (Fig. 2 and 3) were obtained from pressure cooker trials by extraction of the dyed material with Cellosolve–caustic soda–sodium hydrosulphite solutions [10] and determination of the optical density of the extracts on the Hilger Spekker photoelectric absorptiometer.

STABILITY OF ALKALINE LEUCO VAT DYES IN SOLUTION

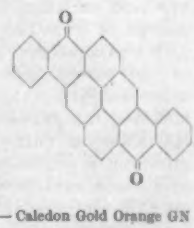
Our knowledge [11,12] of the behaviour of leuco vat dyes at 90°c. in orthodox batch-wise and continuous dyeing systems, and of the influence which the chemical constitution of the dye plays in such well known phenomena as hydrolysis of labile groupings, dehalogenation, isomerisation, and over-reduction, was of the utmost value in forecasting those dyes which would be stable in the reduced state at temperatures of 100–130°c.

The following commercial dyes were found on preliminary testing to be virtually immune from destruction at 130°c. even in the absence of inhibitors or protective agents—

I—Caledon Yellow GN
II—Caledon Gold Orange GN
III—Caledon Red 2G
IV—Caledon Red BN
V—Caledon Violet XBN
VI*a*—Caledon Dark Blue 2R
VI*b*—Caledon Dark Blue G
VI*c*—Caledon Jade Green XBN
VII—Caledon Olive Green B
VIII—Caledon Yellow 5G
IX—Caledon Golden Yellow GK

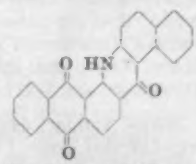


I— Caledon Yellow GN

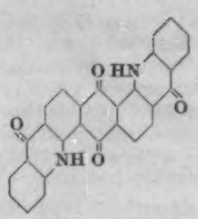


II— Caledon Gold Orange GN

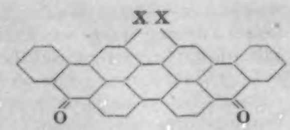
III— Caledon Red 2G



IV— Caledon Red BN



V— Caledon Violet XBN



VIa— Caledon Dark Blue 2R (X = H)

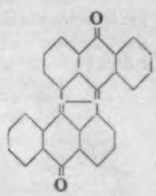
VIb— Caledon Dark Blue G (X–X = $O \cdot CH_2 \cdot CH_2 \cdot O$)

VIc— Caledon Jade Green XBN (X = $O \cdot CH_3$)

It will be observed from the structures of a number of these dyes (I–VIc) that they are relatively compact polynuclear compounds and are free from halogeno, acylamino, pendant aminoanthraquinonoid, and similar labile groupings. Furthermore, these products are similar insofar as most of them can be prepared by fusion processes (often in caustic potash). Such processes naturally demand the use of high temperatures, and many of these dyes are present, on completion of the fusion process, in leuco form in the vehicle of their manufacture.

The short list of dyes given above was extended during this work to include several other dyes and vattable compounds which are not normally considered to be suitable for use as vat dyes for dyeing purposes, e.g. *iso*dibenzanthrone (X), acedianthrone (XI), and Caledon Printing Green 6B (XII), which were also found to be stable.

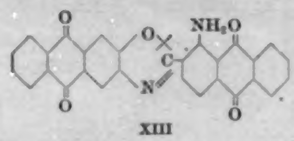
X— *iso*Dibenzanthrone



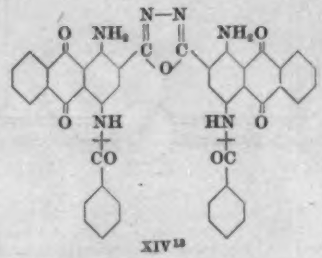
XI— Acedianthrone

The introduction of halogens (e.g. into *iso*dibenzanthrone to yield Caledon Brilliant Purple 4R, into pyranthrone to yield Caledon Orange 2RT, etc.) at once creates problems of change of hue and variation in fastness due to loss of such groupings from the leuco form of the vat dye at high temperatures. Similarly, the leuco derivatives of the parent anthraquinone–carbazole dyes are more stable than the leuco forms of the benzoylated aminoanthraquinone–carbazoles (e.g. Caledon Brown R). Caledon Olive D, because of its pendant grouping, is sensitive to high-temperature reduction conditions, and increasing destruction is observed over the temperature range 60–130°C. On the other hand, Caledon Olive Green B (VII), which may be regarded as the parent of Caledon Olive D, remains virtually unaffected throughout the same temperature range, and this dye possesses no pendant groupings.

Many similar examples could be quoted to support this general theory, but, as is always the case in dye chemistry, there are several exceptions which appear to break the general rule. Examples of these exceptions are XIII and XIV[13]—



XIII



XIV[13]

and it will be seen that they might be expected to suffer decomposition by fission at the C–O or CO–NH bonds (indicated by dotted lines) under high-temperature reduction conditions. In fact it has been found that, under the dyeing conditions employed in the pressure cooker experiments, these compounds are barely affected by treatment at 120°C. Furthermore, they maintain the expected fastness properties and are regarded as suitable for this type of dyeing.

Blue vat dyes present a special problem, since all those derived from indanthrone suffer increasing degrees of molecular damage in leuco form between 60° and 130°C. It is from this group of vat dyes that the brightest and fastest blues are currently available, and sufficiently powerful protective agents have not yet been found to give complete protection to these dyes in reduced form at temperatures in the region of 120°C. New blue vat dyes of the general structure XIV[13], in spite of the possibilities of fission (see above), have shown good stability in caustic soda–sodium hydrosulphite vats at 100–120°C.

PROTECTIVE AGENTS FOR LEUCO DYES

Previous workers [14,15] have shown that certain compounds have a protective effect on temperature-sensitive vat dyes in the reduced form, and the use of such inhibitors has allowed several dyes to be applied at some 30–40°C. above their normal application temperature. It must be realised that the new high-temperature package-dyeing systems may call for temperatures of application of dyes some 60–80°C. higher than normal, and very powerful protective agents will be demanded if the range of available dyes is to be extended by protective techniques. A variety of products, ranging from inorganic nitrites and cobalt salts[14] to certain carbohydrates, have been useful in preventing high-temperature destruction in the form of over-reduction, isomerisation, and dehalogenation at temperatures in the region of 90°C.,

TABLE I

Behaviour of Protective Agents at 120°C.

	Inhibitor	Concn. (g./litre)	Observed Effect, relative to Control Dyeing applied at Normal Temp. — Caledon Gold Orange 3G	Caledon Blue XRC
1.	No inhibitor—high temp.	—	Redder and duller dyeing	Very much weaker, unlevel grey dyeing
2.	Sodium nitrite	2·5–5·0	Partial protective effect; resultant dyeing much weaker and a little redder	Partial protective effect; resultant dyeing blue, but greener and weaker
3.	Cobaltous acetate	2·5–5·0	Partial protective effect; resultant dyeing much weaker	Partial protective effect; resultant dyeing blue, but greener and much weaker
4.	Sodium cobaltinitrite	2·5–5·0	Partial protective effect; resultant dyeing very much weaker	Partial protective effect; resultant dyeing bluer, but greener and weaker
5.	White dextrin (required extra NaOH)	2·5–5·0	No significant improvement	No significant improvement
6.	Glucose syrup 50%	5–10	Partial protective effect; resultant dyeing a little weaker and a little duller	Partial protective effect; resultant dyeing blue, but a little greener and a little weaker
7.	Maltose	2·5–5·0	Partial protective effect; resultant dyeing a little duller at 2·5 g./litre. Higher concn. yield weaker dyeings	Partial protective effect; resultant dyeing blue, but a little greener and a little weaker
8.	Cellulose sulphite lye	2·5–5·0	No significant improvement	No significant improvement
9.	Cellofas B (ICI)	2·5–5·0	No significant improvement	No significant improvement

and it was considered necessary to investigate the value of such products at 120°C. The results of the present tests carried out on two sensitive dyes, viz. Caledon Gold Orange 3G and Caledon Blue XRC, are shown in Table I. Dyeings for these tests were made in the pressure cooker at 120°C. over a range of caustic soda–sodium hydrosulphite concentrations. The dyeings were held for 15 min. at 120°C. and then cooled back to 50°C. over a period of 30 min.

It will be observed from Table I that white dextrin, Cellofas B, and sulphite cellulose lye are of no practical value with these two dyes under the present conditions of dyeing. Cobalt acetate and sodium cobaltinitrite do exert a positive protective effect but appear to be of little practical value. Sodium nitrite exerts a more positive effect than the cobalt compounds, but the improvement obtained is not enough to make it worthy of adoption in the case of these two dyes. Maltose and glucose also give positive protective action with the two dyes in question, but because their protective effect is incomplete and simultaneously affects the tinctorial yield adversely, it would be necessary to carry out much more experimental work before recommending their adoption. Glucose shows the most promise.

Experiments with the same range of products on a leuco-stable vat dye, viz. Durindone Orange R, showed that the various agents improved the tinctorial yield. Thus 10 g. glucose (50%) per litre with the dye in question yielded greater tinctorial value than a dyeing made without addition; the electrolyte sodium nitrite, however, had appreciably less effect on the tinctorial value; maltose only gave a slight advantage towards greater depth of colour. Observations of this kind suggest that reduction-damage inhibitors may markedly influence the behaviour of stable vat dyes, and the present work suggests that it will be necessary to search for fundamental reasons to explain the mechanism of protective agents before products effective at 100–130°C. are found.

THE BEHAVIOUR OF REDUCING AGENTS AT HIGH TEMPERATURE

The reducing efficiency of sodium hydrosulphite in caustic soda solution rapidly falls in the presence of air and reducible substances. Orthodox package-dyeing equipment is invariably open to the atmosphere at some point, and additions of small quantities of hydrosulphite to the dye liquors are often found to be necessary. It was reasonable to expect, therefore, that dyeing in the totally enclosed high-temperature machine would require a somewhat lower hydrosulphite consumption. This is, of course, difficult to prove under laboratory conditions, but it was found that, although no additions of hydrosulphite were required during the dyeing operation, it was not possible to reduce the recommended quantities for vatting and dyeing a given product by more than 10–15% without adverse effect.

The reducing agents Formosul and formamidine-sulphinic acid (thiourea dioxide) were compared with sodium hydrosulphite, since it was thought that their greater stability at high temperatures might render them useful for this type of dyeing.

TABLE II

Effect of Dyeing Temperature on the Tenacity of Bleached Mercerised Cotton Yarn

Sample	Count	Dry Tests		Wet Tests		Fluidity
		Extension (%)	Change in Product of Count × Strength (%)*	Extension (%)	Change in Product of Count × Strength (%)*	
Undyed	13·1	7	0	10	0	3·6
Dyed at 50°C.	12·6	8	+3·4	10	−1·0	3·9
Dyed at 120°C.	12·5	9	+4·5	10	−2·8	3·6

*Average values for 25 tests.

In general it was found, however, that both these products, particularly with the dye structures XIII and XIV, were more active in bringing about dye decomposition. The bright red oxazole dye XIII gave much yellower dyeings (indicating decomposition) with Formosul than were obtained with either sodium hydrosulphite or formamidine-sulphinic acid. Blue dyes of the type XIV yielded greys with the latter agent, but gave the correct colour with both hydrosulphite and Formosul. Thus at this stage there appears to be little point in replacing sodium hydrosulphite as a reducing agent for this process of dyeing.

EFFECT OF CAUSTIC ALKALINE REDUCING SOLUTIONS ON CELLULOSE AT HIGH TEMPERATURES

No experimental evidence has been provided to show that the swelling of natural or regenerated cellulose in dilute baths of caustic soda, sodium hydrosulphite, and vat dye is greater or less at 120° than at 60°C. Such information would be necessary before deciding whether a given fibre or package to be dyed is in its most receptive state at high or at low temperature.

Butterworth[2] has shown that vat-dye liquors at 120°C. have an adverse effect on viscose rayon, and records dry strength losses of 10–20% and wet strength losses of 20–30% in viscose rayon dyed with vat dyes at high temperatures. He did not condemn the dyeing process out of hand, but it is obvious that treatment of this fibre at temperatures greater than 100°C. must be of short duration if the qualities of the fibre are to be preserved. The more robust cotton fibre is known to withstand strongly alkaline pressure boils in preparative processes without adverse effect on its textile qualities. It is not anticipated that troubles due to damage to the cotton fibre will arise from the proposed new processes. Random measurements have shown that yarn which has been vat-dyed at 120°C. shows no significant difference in tenacity or change in fluidity values (see Table II) when compared with yarn dyed at 50°C.

BEHAVIOUR OF THERMOSTABLE LEUCO VAT DYES TOWARDS CELLULOSE AT ELEVATED TEMPERATURES

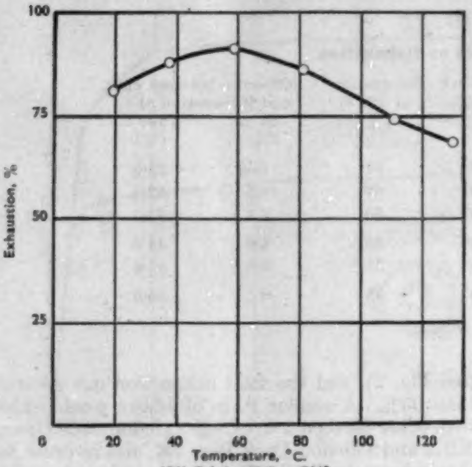
The effect of dyeing temperatures on the levelness of vat dyeings produced on cellulosic fibres under orthodox dyeing conditions has been the subject of much study. The value of temperature control is often underestimated, but in recent years there has been a more general adoption of "gradual temperature rise" processes and of the use of higher temperatures than normal to promote better levelling.

The rate of dyeing of Method 2 (50°C.) dyes can be retarded by dyeing at 20–30°C. and subsequently raising the temperature slowly to 50°C., but beneficial effects are small. Likewise, when the leuco solubility of the Method 1 dyes will permit it, greater control of the rate of dyeing can be obtained by dyeing at a low temperature, and then raising gradually (e.g. 1°C. per minute) to the normal temperature. On the other hand, promotion of levelling of Method 1 and Method 2 dyes can be obtained by taking the temperature some 10–30°C higher than normal, which decreases affinity and increases rate of migration. The effectiveness in practice of such a technique is limited by the small temperature range, and furthermore the chemical stability of the dyes will not permit its wholesale adoption.

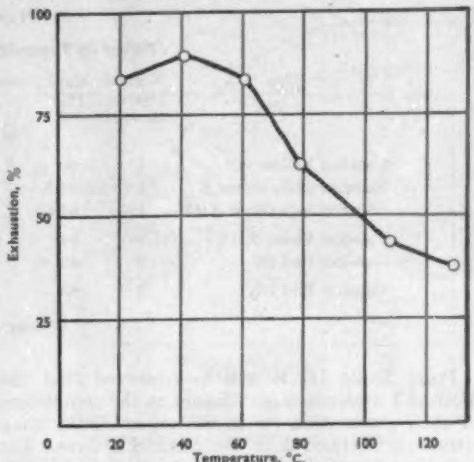
The migration and the affinity of dyes from the Method 2 (cold) and Method 3 classes are similarly affected by dyeing at 30–40°C. and cooling gradually to 20°C. in order to obtain maximum tinctorial value in the available dyeing time. Few dyeing machines are, however, fitted with adequate cooling systems, and this has retarded employment of such a technique.

A series of temperature–exhaustion curves were prepared showing the percentage exhaustion of dyebaths at 20, 40, 60, 80, 110, and 130°C. by dyeing on bleached cotton yarn at a liquor ratio of 30 : 1 for 40 min. The percentage exhaustion was determined optically (see p. 81), and a representative series of curves are shown in Fig. 2 and 3. It will be observed that, in all cases, the percentage exhaustion falls appreciably below the maximum point when working between 60° and 130°C. All the dyes represented show similar curves, i.e. descending with increasing temperature above 60°C. For convenience the data for the curves in Fig. 2 and 3 are analysed in Table III.

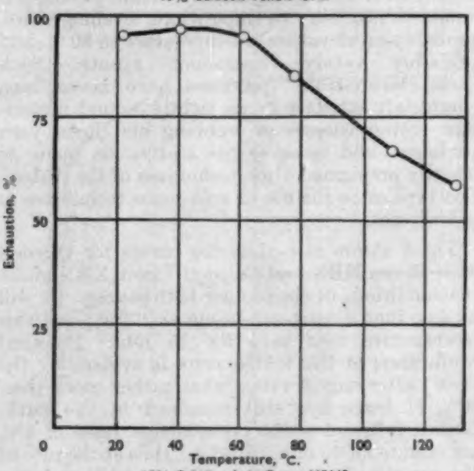
The values in the last column show clearly that the exhaustion of the dyebath is always much less at 130°C. than at the temperature of maximum exhaustion, and consequently it seems logical to commence dyeing at high temperatures, viz. 110–130°C., and then cool back gradually to the temperature of maximum affinity.



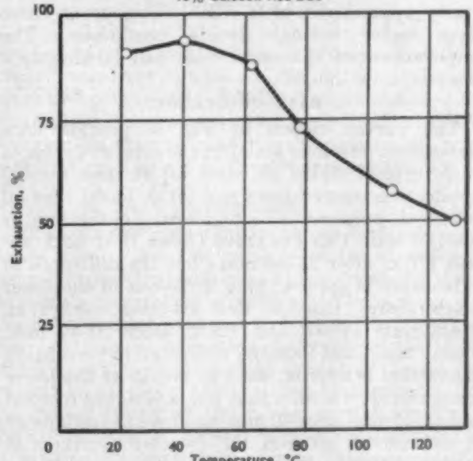
15% Caledon Yellow GNS



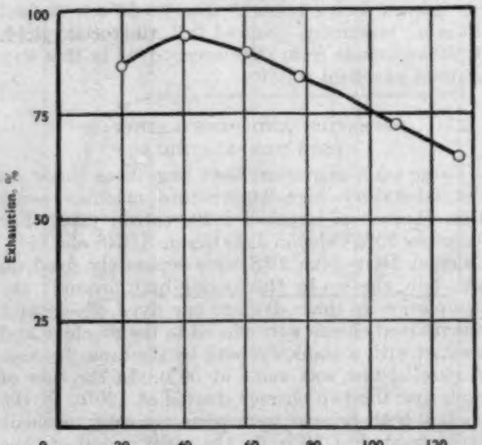
15% Caledon Red 2GS



15% Caledon Jade Green XBNS



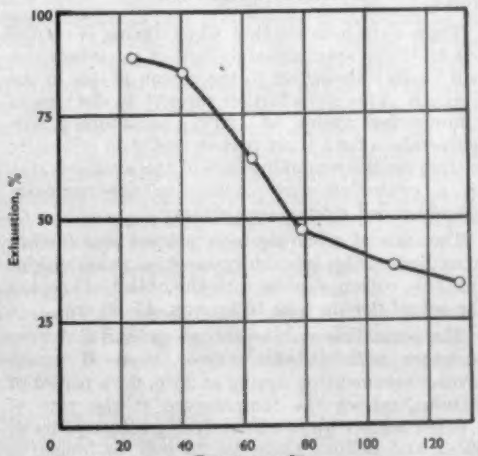
20% Caledon Violet XBNS



15%Caledon Olive Green BS

Bleached 2/20s cotton yarn
Liquor ratio 30 : 1 40 min.
No salt addition

FIG. 2



20% Caledon Red BNS

Bleached 2/20s cotton yarn
Liquor ratio 30 : 1 40 min.
No salt addition

FIG. 3

TABLE III

Effect of Temperature on Exhaustion

Dye	Normal Dyeing Method	Max. Exhaustion* (%)	Max. Exhaustion* Temp. (°c.)	Exhaustion* at 130°c. (%)	Difference between Max. and Exhaustion at— 20°c. (%)	Difference between Max. and Exhaustion at— 130°c. (%)
Caledon Yellow GN ...	1	90	60°	67	10·0	23·0
Caledon Olive Green B	1	94·5	40°	62	8·5	32·5
Caledon Jade Green XBN	1	97·5	40°	60	2·5	37·5
Caledon Violet XBN ...	2	94	40°	50	4·0	44·0
Caledon Red 2G ...	2	89	40°	38	5·0	51·0
Caledon Red BN ...	3	90	20°	35	0	55·0

* Dyeing time 40 min.

From Table III it will be observed that the Method 1 dyes are more efficient in the completion of their exhaustion on to cotton at 130°c. than either the Method 2 or the Method 3 dyes. The latter are least efficient in this respect, and this is easily appreciated from the behaviour of these dyes under normal dyeing conditions. The implications of this behaviour will be discussed later.

RATE OF DYEING

The curves shown in Fig. 4 provide data (laboratory-machine scale) on the rates of dyeing of three typical stable vat dyes (*a*) at their normal application temperatures and (*b*) at 120°c. For all practical purposes a commercial equilibrium is reached with Caledon Olive Green B at both 50° and 120°c. after 20–40 min., but the difference in exhaustion is approx. 35% in favour of the lower temperature. Caledon Red 2G also reaches an equilibrium at 50° and 120°c. after 20–40 min. dyeing time, and here the difference in percentage exhaustion is approx. 45% in favour of the lower temperature. Caledon Red BN, again, has reached an equilibrium after 40 min. and here the difference in exhaustion between the two temperatures is approx. 45% in favour of the low-temperature dyeing.

These data indicate that when dyeing is carried out at 120°c. approximately half of the dye which will finally exhaust on to the cotton is still in the dyebath. This gives further support to the idea of commencing dyeing at 120°c., maintaining this temperature for a short period, and then gradually feeding on the remaining half of the available dye by a controlled slow cooling to the normally recommended dyeing temperature.

The idea of a cooling-bath process was further examined on the laboratory machine using one or two 1-lb. cotton cheeses with the object of keeping the actual dyeing time to approx. 45–60 min.

The normal rising-temperature process of dyeing packages with Caledon Olive Green B would involve commencing dyeing at 25°c. for a period of 20 min., raising the temperature at the rate of 1°c. per minute up to a final dyeing temperature of 50°c., and holding there for 20 min. or longer in order to obtain a level result. The total dyeing time would therefore be a little over one hour. The initial exhaustion at 25°c. would be approx. 90% (see Fig. 2), and the final exhaustion not greater than 95%. A similar state of affairs would exist with other Method 1 dyes, e.g. Caledon Jade Green XBN and Caledon Dark Blue 2R, and in order to obtain level dyeings on densely wound packages it would be necessary to employ long levelling times, probably an elevation in temperature to 80°c., and probably vat-dye restraining agents. Such "temperature-scale" processes have never been completely satisfactory on tightly wound mercerised cotton cheeses or webbing and linen yarn packages, and recourse has had to be made to lengthy prepigmentation techniques of the Abbot–Cox type or to the use of acid–leuco techniques in pale shades.

Fig. 5 shows rate-of-dyeing curves for Caledon Jade Green XBN and Caledon Violet XBN under the conditions of the cooling-bath process. It will be seen that dyeing was begun at 120°c., and this temperature then held for 15 min. Practical equilibrium at this temperature is evident by the "flat" after only 5 min., when rather more than 50% of leuco dye still remained in the bath. Cooling followed at the approximate rates of 4°c. per minute for 10 min. (to 80°c.), then at the rate of 2°c. per min. for 10 min. (to 60°c.), and then 1·5°c. per minute for a further 10 min. (to 45°c.). A final 15 min. treatment ensured full tinctorial yield. Knittings made from the cheeses dyed in this way showed excellent solidity.

MIGRATION AND PENETRATION AT HIGH TEMPERATURES

Large-scale migration tests have been made on the laboratory high-temperature machine using 1-lb. cheeses of bleached 2/20s cotton yarn. For example, 30% Caledon Jade Green XBNS and 15% Caledon Dark Blue 2RS were separately dyed on two 1-lb. cheeses by the cooling-bath process. On completion of these dyeings one dyed cheese and one undyed cheese were placed in the machine and treated with a blank dyebath by the same process. A parallel test was made at 50°c. In the case of each dye, the two cheeses treated at 120°c. by the cooling-bath process were perfectly solid, whereas those treated at 50°c. for the same period of time showed very poor levelling.

Dyeings carried out by the cooling-bath process (commencing at 120°c.) on 3/36s grey mercerised

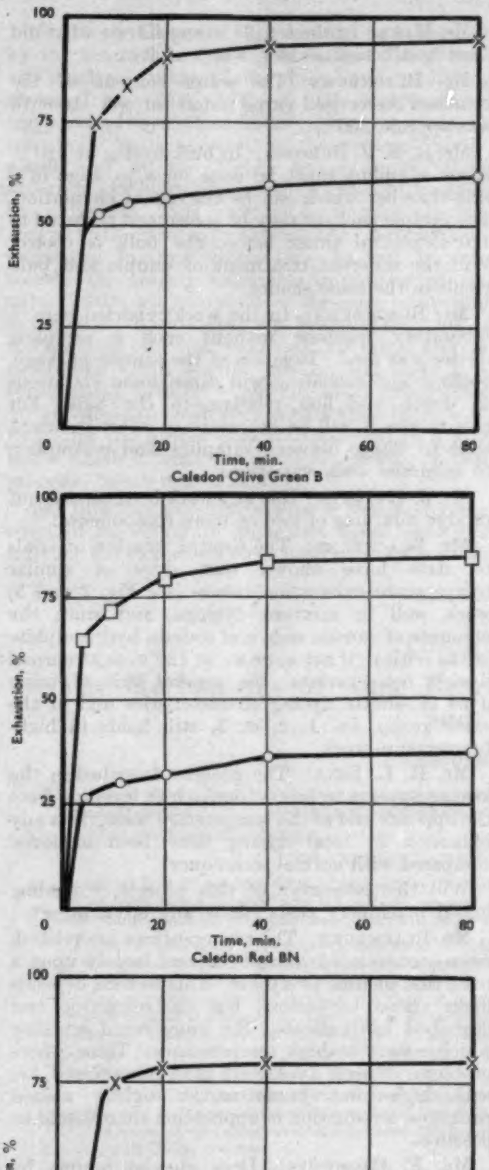


FIG. 4

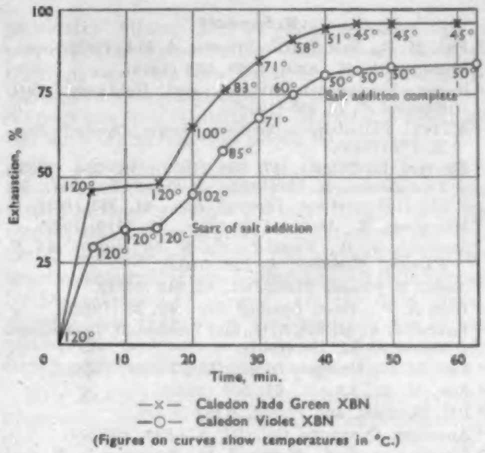


FIG. 5—Cooling-bath Process (Cheeses dyed in high-temperature machine)

sewing yarn in tightly wound cheeses were free from "cross-over" whites and the individual threads were well penetrated. Parallel dyeings obtained by the normal leuco process on the same quality of yarn showed marked "cross-overs", relatively poor penetration, and a slightly stronger appearance.

Discussion

It has been shown that leuco vat dyes possess a lower affinity for the cellulosic fibres at temperatures higher than normal, which results in more favourable migration conditions. There is as yet no experimental evidence to suggest that marked fibre swelling or molecular dispersion of the leuco dye play a significant part in increasing the rate of migration at 120°C. The cooling-bath process, i.e. beginning dyeing at 120°C. and cooling slowly to 50°C., enables a greater degree of control of dyebath exhaustion to be achieved than is possible over more limited temperature ranges. Final dyebath exhaustion approaches that obtained in normal practice as a result of cooling to the normally recommended dyeing temperature. Although much practical work remains to be done, it is apparent that the high-temperature dyeing process for leuco-stable vat dyes minimises the problems of unlevel dyeing, particularly those created by hard-twist yarns and tightly wound packages. The possibility of vat dyeing linen yarns and cotton tapes in package form at temperatures greater than 100°C. must not be overlooked.

The dye chemist is faced with the problems of producing a wider range of stable vat dyes or alternatively the probably more difficult research target of finding agents which will adequately stabilise leuco vat dyes at the high temperatures involved.

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(*MS. received 16th June 1954*)

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Discussion

Mr. B. KRAMRISCH: Have the lecturers made any comparison between the fastness properties, e.g. to light, washing, and bleaching, of high-temperature dyeings of vat dyes and of those prepared by orthodox dyeing methods?

Mr. BLACKBURN: In addition to the colour and tinctorial yield obtained, the main criterion in the selection of stable vat dyes has been the maintenance of normal light and wet fastness properties.

Mr. L. MORRIS: What is the effect of using grey cotton? Does the extraction of non-cellulosic constituents interfere?

Mr. BLACKBURN: When grey mercerised sewing yarns have been dyed there has been no significant effect due to the simultaneous purification and dyeing of the cotton. Adverse effects, revealed by dullness of colour on the outsides of five-ply grey webbing-yarn packages scoured at normal temperature and dyed at 120°C., have, however, been experienced. Prescouring of such yarns at a temperature at least equal to that used in the subsequent dyeing operations eliminated this defect.

Mr. G. S. MARR: Referring to the cotton impurities affecting the dyeings, it should be noted that these impurities are not constant; e.g. in the case of good Egyptian yarn these impurities were natural, but in the case of condenser-type yarn they were unnatural, being not far removed from paraffin oil.

Was the bleached yarn used in the test dyeings obtained from ordinary commercial sources or from laboratory processing? If the latter, would there not be the possibility of cellulosic degradation in the case of commercially bleached yarn under the strongly alkaline conditions at 120°C. and corresponding pressure?

Mr. BLACKBURN: All yarns employed were obtained from commercial sources, and in addition to the results recorded in Table II, no evidence of degradation of bleached and grey mercerised yarns has been detected.

Mr. MARR: In the tensile strength tests what did "wet test" mean—how wet was it?

Mr. BLACKBURN: The water content of the bleached mercerised yarns tested for wet strength was approx. 200%.

Mr. R. E. B. BURGESS: In bulk dyeing at 120°C. shade sampling must be done on a package in a side-chamber which can be cut out of circulation. The sample package may be cooled and reheated to 120°C. several times before the bulk is cooled. Will the different treatment of sample and bulk result in the same shade?

Mr. BLACKBURN: In the work reported here, a laboratory machine without such a sampling device was used. Isolation of the sample package, cooling, and reheating will cause some variations in depth and hue relative to the bulk. For this reason it will be necessary to allow sufficient time to elapse between sampling and resampling to minimise such variations.

Mr. J. KUPCZYK: Has any work been carried out on dye mixtures of two or more components?

Mr. BLACKBURN: The limited number of trials to date have shown that dyes of similar temperature-exhaustion curves (see Fig. 2 and 3) work well in mixture dyeings, and since the amounts of caustic soda and sodium hydrosulphite are as critical, if not more so, at 120°C. as at normal dyeing temperatures, the general rule of using dyes of similar dyeing characteristics and of the same group, i.e. 1, 2, or 3, still holds in high-temperature work.

Mr. R. L. BELL: The process described in the lecture appears to be an approach to levelling from the opposite end of the temperature scale. Has any reduction in total dyeing time been achieved compared with normal techniques?

Will the economics of this process, excluding initial machinery costs, show any advantages?

Mr. BLACKBURN: The two questions are related, since economic advantages depend largely upon a reduction in time of dyeing. This in turn depends upon numerous factors, but the migration test described has indicated the more rapid levelling which occurs at high temperatures. Thus, where problems of level dyeing are most pronounced, i.e. with high-count yarns and/or tightly wound packages, a reduction in application time should be possible.

Mr. F. CROMPTON: Does glucose inhibit by forming a reducing agent with surplus caustic soda?

Mr. BLACKBURN: We are aware that glucose can form addition products with sodium hydrosulphite, and it is our opinion—without experimental proof—that the glucose complexes in the dye vat, thus inhibiting the action of excess hydrosulphite at any one time and in this way preventing leuco-dye damage by over-reduction.

Mr. CROMPTON: Does the use of cobalt form oxycellulose?

Mr. BLACKBURN: The limited experiments with cobalt salts have not given any indication of oxycellulose formation.

Mr. H. A. TURNER: One interesting statement by the lecturers is that soluble sugars like glucose and maltose protect the dye from modifying chemical reactions at these high temperatures. One has always thought of these reactions as essentially reducing, and, in the presence of the alkali and at the higher temperatures, these sugars might have been expected to contribute to the reduction. This leads me to wonder whether, contrary to first expectation, the carbohydrate impurities in grey cotton or—to put it even wider—the readily oxidisable impurities of the natural fibre, can also stabilise the leuco compound in the bath. I know that Mr. Morris is thinking of the resisting effect of wax, and this might have a substantial effect on dye uptake, but there is a considerably greater weight of alkali-extractable carbohydrate in clean grey cotton than there is of wax, and the former goes into solution in a kier boil—which is what the goods are getting in this process—much more readily.

Mr. BLACKBURN: The evidence concerning the effect of carbohydrate impurities upon leuco dye stability shows that cellulose itself exerts a positive protective effect, but sulphite cellulose lye—essentially a lignocellulose—has shown no such effect in our tests (see Table I). It is difficult to visualise a combination of dye and glucose which corresponds to a combination of dye and cellulose, but such a combination might be possible.

Mr. TURNER*: On second thoughts, I wonder whether atmospheric oxygen is completely excluded in these pressure dyeings. If not, then, for certain dyes, a destructive oxidation of the dye itself, commencing from the oxidation of the leuco compound, might be discouraged or inhibited by the presence of glucose. On the data given, showing that there is no distinct tendering of the cotton, this does not seem likely, but have similar tests for fibre modification been made for all dyes?

Mr. BLACKBURN*: Air is entrapped in the apparatus, but dye decomposition experienced to date has always been consistent with over-reduction and not destructive oxidation. We have no evidence of significant differences in the results of fibre modification tests on cotton, which involve a limited number of dyes only.

* Communicated.

COMMUNICATION

The Mechanisms of some Reactions between *N*-Halogenoamines and Wool*

CHRISTOPHER EARLAND

It is shown that the reactions occurring between wool and *N*-halogenoamines do not proceed by common mechanisms. Although these reactions are complex, it is concluded that—

(a) *N*-Chlorourea diffuses into the fibre, where the chlorine produced by the equilibrium—

$$NH_2{\cdot}CO{\cdot}NHCl + H^+ + Cl^- \rightleftharpoons NH_2{\cdot}CO{\cdot}NH_2 + Cl_2$$

reacts with the keratin. This explains why the properties of the wool after reaction with *N*-chlorourea differ from those of wool which has been treated with chlorine in acid solution, since under the latter conditions reaction proceeds from the outside to the interior of the fibre.

(b) It has been shown previously that *N*-chlorosulphamic acid enters into reactions with wool in acid solution, although reactions that confer unshrinkability occur only in presence of chloride ions at high concentration. Kinetic studies indicate that the rate-determining step in these reactions is the ion-exchange process that determines the rate of access of the *N*-chlorosulphamic acid to the wool. The overall rate of the reactions occurring is accordingly reduced by increasing the concentration of anions, including chloride ions, in the solution. Examination of a number of anions, other than chloride, as possible promoters of the anti-shrink reaction indicates that nitrate also is a promoter, though much less effective than chloride.

(c) The high concentrations of free bromine which are produced when solutions of *N*-bromoacetamide and *N*-bromosuccinimide react with wool show that these reactions are essentially brominations. In the initial stages direct reaction between the bromamines and wool is possible, the rate-controlling factor being a diffusion process.

Introduction

The optimum conditions for rendering wool non-felting with certain *N*-halogenoamines have been determined[1–3] and these may be summarised as follows—(a) *N*-Chlorourea $NH_2{\cdot}CO{\cdot}NHCl$ and *N*-chlorosulphamic acid $NHCl{\cdot}SO_3H$ must be employed in solution of pH less than 2 in the presence of a high concentration of chloride ions. In the absence of high concentrations of these ions reaction still occurs, but the wool does not become shrink-resistant unless very high concentrations of chloramine are employed. (b) *N*-Bromoacetamide must be applied from solution below pH 2, and *N*-bromosuccinimide from solution below pH 4. With these bromamines the addition of salts to their solutions is unnecessary.

The present work is confined to the mechanisms of the heterogeneous reactions between the above four compounds and wool. The reactions of halogenoamines in solution have been studied in considerable detail and a number of mechanisms proposed. It is generally accepted that, in their reactions in hydroxylic solvents with halogen acids as catalysts, free halogens are

* The term "*N*-halogenoamine" as used in this work embraces compounds containing the N–Hal group in general, and is not restricted to halogen derivatives of amines.

usually concerned as intermediates [4]. Thus, the rearrangement of *N*-chloroacetanilide in water with hydrogen and chloride ions as catalysts has been shown to proceed via the following steps [5]—

$$C_6H_5{\cdot}NCl{\cdot}CO{\cdot}CH_3 + H^+ + Cl^- \rightarrow C_6H_5{\cdot}NH{\cdot}CO{\cdot}CH_3 + Cl_2$$
$$C_6H_5{\cdot}NH{\cdot}CO{\cdot}CH_3 + Cl_2 \rightarrow Cl{\cdot}C_6H_4{\cdot}NH{\cdot}CO{\cdot}CH_3 + H^+ + Cl^-$$

Likhosherstov [6] has postulated a similar mechanism for the chlorination of phenol by *NN'*-dichlorourea—

$$CO(NHCl)_2 + 2H_2O \rightarrow CO(NH_2)_2 + 2HOCl$$
$$HOCl + H^+ + Cl^- \rightarrow H_2O + Cl_2$$
$$C_6H_5OH + Cl_2 \rightarrow Cl{\cdot}C_6H_4{\cdot}OH + H^+ + Cl^-$$

On the other hand, Hurst and Soper [7] have concluded that the chlorination of phenols by *N*-chloroacetanilide does not proceed exclusively by the intermediate production of hypochlorous acid but partly by direct interaction. The conclusions of Bell [8], however, that the rearrangement of *N*-bromoacetanilide in non-dissociating solvents with general acid catalysis is truly intramolecular, as is the nitramine rearrangement [9]—

$$C_6H_5{\cdot}NH{\cdot}NO_2 \rightarrow o\text{-}NO_2{\cdot}C_6H_4{\cdot}NH_2$$

must be doubted. Although Bell was unable to detect free halogen in the reacting system, it is possible that the reaction proceeds by the intermediate formation of a free brominating agent. Thus, it has been shown that *N*:2:4:6-tetrabromoacetanilide in chlorobenzene with acetic acid as catalyst may be used to brominate anisole and phenetole, the reaction proceeding via the intermediate formation of bromine acetate [10].

Further information on reaction mechanisms involving halogenoamines is given in a review by de la Mare [11].

Previous work on reactions between chloramines and wool has failed to elucidate their exact mechanism, although it has been shown that the very small amount of chlorine in equilibrium with a solution of a chloramine—

$$R{\cdot}NHCl + H^+ + Cl^- \rightleftharpoons R{\cdot}NH_2 + Cl_2$$

does not effect a simple chlorination of the wool [12]. The properties of the treated wool have confirmed this view. *N*-Bromoacetamide and *N*-bromosuccinimide, however, do react with wool largely through the intermediate formation of free halogen [3]. The mechanism whereby the latter reaction is initiated is rather obscure.

N-Halogenoamines vary widely in chemical properties; e.g. *N*-chlorosulphamic acid is a strong acid and may be titrated with wool, whereas *N*-chlorourea and the bromamines under consideration are neutral molecules. It is therefore unlikely that these substances will react with wool by identical mechanisms, and the experimental data presented here, together with other data published previously [1–3, 12], have been examined from this viewpoint.

Experimental

The materials and the experimental procedures used were as described previously [1–3, 12]. Unless stated otherwise, *N*-chlorosulphamic acid and *N*-chlorourea were applied to the wool at concentrations equivalent to 4·0% available chlorine, calculated on the weight of the fabric, in 0·50% (wt./vol.) sulphuric acid solution at 40°c. at a liquor : wool ratio of 80 : 1. The fabric was fitted on to a stirrer revolving at 100 r.p.m., and the time taken for half the oxidising power of the solution to disappear was determined. Since the reactions are pseudo-unimolecular, this is a convenient measure of the rate of the reaction.

Shrinkage testing was performed by hand-milling fully relaxed patterns of fabric [2, 13], and chlorine analyses were made by Drs. Weiler and Strauss of Oxford on wool patterns which had received various treatments and had then been Soxhlet-extracted with water for 27 hr.

Reactions between chloramines and phenol were performed as described previously [13], and where these were carried out in the presence of salts, 10·0% (wt./vol.) of the anhydrous salt was added to the solution.

I— Reactions between Wool and *N*-Chloramines

Results

1. INFLUENCE OF ACID AND CHLORIDE CONCENTRATIONS ON THE RATE OF THE REACTION

It has been established previously [2] that the acid and sodium chloride concentrations of an effective shrinkproofing solution of *N*-chlorourea or *N*-chlorosulphamic acid are interrelated; i.e. as the concentration of one ion is reduced the other must be increased for the solution to be still capable of rendering fabric non-felting.

Tables I–III show how the rate of the reaction between wool and these two chloramines changes when the concentrations of sodium chloride and acid in the solution are varied.

TABLE I

Effect of Acid and Chloride Concentrations on the Rate of Reaction between *N*-Chlorourea and Wool

NaCl Concn. (% wt./vol.)	H_2SO_4 Concn. (% wt./vol.)	Half-life ($t_{\frac{1}{2}}$ min.)	$\sqrt{H_2SO_4 \text{ Concn.}} \times t_{\frac{1}{2}}$
0	0·10	>250	>79
0	0·20	~170	~76
0	0·50	90	63·7
0	1·00	60	60·0
5·0	0·10	30	9·5
5·0	0·20	19	8·5
5·0	0·50	11	7·8
5·0	1·00	8	8·0
10·0	0·10	24	7·6
10·0	0·20	13	5·8
10·0	0·50	10	7·1
10·0	1·00	8	8·0

TABLE II

Effect of Chloride Concentration on the Rate of Reaction between *N*-Chlorourea and Wool in 0·092% Hydrochloric Acid

NaCl Concn. (% wt./vol.)	Half-life ($t_{\frac{1}{2}}$ min.)	$\sqrt{\text{NaCl Concn.}} \times t_{\frac{1}{2}}$
2·0	35	49·4
4·0	25·5	51·0
6·0	21·5	52·7
8·0	17	48·1
10·0	15	47·4
12·0	13	45·0

TABLE III

Effect of Acid and Chloride Concentrations on the Rate of Reaction between *N*-Chlorosulphamic Acid and Wool

NaCl Concn. (%wt./vol.)	H_2SO_4 Concn. (%wt./vol.)	Half-life ($t_{\frac{1}{2}}$ min.)
0	0·10	8
0	0·20	8
0	0·50	7
0	1·00	6
5·0	0·10	14
5·0	0·20	11
5·0	0·50	10
5·0	1·00	8
10·0	0·10	18
10·0	0·20	13
10·0	0·50	10
10·0	1·00	9

The results given in Tables I–III show that there is a fundamental difference in the kinetics of the reactions between wool and the two chloramines. Whereas the rate of the reaction between *N*-chlorourea and wool is increased by both chloride and hydrogen ions, that between *N*-chlorosulphamic acid and wool is increased to a lesser degree by hydrogen ions and is actually reduced by chloride ions.

This suggests that the equilibrium—

$$NH_2{\cdot}CO{\cdot}NHCl + H^+ + Cl^- \rightleftharpoons NH_2{\cdot}CO{\cdot}NH_2 + Cl_2$$

must be concerned in the reaction between *N*-chlorourea and wool.

2. INFLUENCE OF UREA ON THE RATE OF REACTION OF *N*-CHLOROUREA WITH WOOL

If the reaction between *N*-chlorourea and wool proceeds by continual disturbance of the above equilibrium by reaction of the chlorine with the wool, then the addition of an excess of urea should retard the reaction rate (Table IV).

TABLE IV

Effect of Urea on the Reaction between Wool and *N*-Chlorourea

(0·50% H_2SO_4 + 10·0% NaCl soln.)

Urea Concn. (M.)	Half-life ($t_{\frac{1}{2}}$ min.)	$\frac{t_{\frac{1}{2}}}{[\text{Urea}]}$
0·1	10	100
1	16	16·0
2	22	11·0
3	32	10·7
4	42	10·5
5	60	12·0

It is seen from Table IV that for high concentrations of urea the ratio of half-life to urea concentration is constant. This is good evidence that the chloramine–chlorine equilibrium is an important factor in the reaction of *N*-chlorourea with wool, and it need not conflict with the previously held view that the reaction between wool and chloramines does not proceed via free chlorine in solution (see p. 93).

In view of the fact that the slow reaction which occurs between wool and *N*-chlorourea in the absence of chloride ions does not render fabric non-felting [2], fabric treated in the presence of 5 M. urea and 10·0% sodium chloride was tested for shrink-resistance. Again, the slow reaction produced no resistance to milling shrinkage.

3. INFLUENCE OF SALTS ON THE REACTIONS BETWEEN *N*-CHLORAMINES AND WOOL

In Table V is shown the effect of different salts on the rate of the reaction between *N*-chlorourea and wool. The concentration of the salt was equivalent to 10·0% (wt./vol.) anhydrous salt in solution. The milling shrinkages of the patterns after treatment also are given.

TABLE V

Effect of Salts on the Reaction between *N*-Chlorourea and Wool

Salt added	Half-life ($t_{\frac{1}{2}}$ min.)	Area Shrinkage (%) of Pattern	
		Treated	Untreated
None ...	90	—	—
NaCl ...	10	−2·9	29·0
KNO_3 ...	60	32·8	32·3
$MgSO_4$ ...	>120	—	—

It is seen that, although nitrate ions have a slight influence on the rate of reaction, the treated fabric is not unshrinkable.

The effect of a series of anions on the reaction between *N*-chlorosulphamic acid and wool was then investigated (Table VI). In view of the interesting result that nitrate ions promote resistance to milling shrinkage of the treated wool, the salt effect was investigated in more detail than in the corresponding reaction between *N*-chlorourea and wool.

TABLE VI

Effect of Salts on the Reaction between *N*-Chlorosulphamic Acid and Wool

Salt added	pH of Soln.	Half-life ($t_{\frac{1}{2}}$ min.)	Area Shrinkage (%) Treated	Area Shrinkage (%) Untreated
None	1·4	10	24·7	28·7
NaCl	1·4	11	−4·3	26·8
$NaNO_3$	1·4	27	4·6	26·8
KNO_3	1·4	27	6·9	23·9
KF	5·3	>120	—	—
$MgSO_4$	1·4	30	22·7	26·8
$Mg(ClO_4)_2$ ...	1·0	50	11·8	31·2
Na *m*-xylene-4-sulphonate	1·3	50	12·0	31·2
Na naphthalene-*β*-sulphonate	1·1	60	15·3	31·2

It is seen that all the anions investigated reduced the rate of reaction between *N*-chlorosulphamic acid and wool, and only in the case of fluoride ions could this be due to their increasing the pH of the *N*-chlorosulphamic acid solution.

In view of the fact that, after the chloride ion, the nitrate ion is the most effective anion for promoting unshrinkability of fabric treated with *N*-chlorosulphamic acid, a closer comparison of the effects of these anions on the reactions was made. The data given in Table VII were obtained from reactions performed in the presence of 10·0% (wt./vol.) sodium chloride or potassium nitrate in solution.

TABLE VII

Reaction of Wool with *N*-Chlorosulphamic Acid in the presence of Chloride or Nitrate Ions

Available Cl_2* (% on wt. of wool)	Salt added	Half-life ($t_{\frac{1}{2}}$ min.)	Area Shrinkage (%) Treated	Untreated
4·0	None	8	18·2	30·2
4·0	NaCl	10	−2·2	30·2
4·0	KNO_3	26	7·0	30·2
3·0	None	8	23·7	30·2
3·0	NaCl	11	−2·9	30·2
3·0	KNO_3	22	7·0	30·2
2·0	None	8	25·2	29·8
2·0	NaCl	11	−4·0	29·8
2·0	KNO_3	24	15·6	29·8

* As *N*-chlorosulphamic acid

The independence of half-life on the initial concentration of available chlorine shows the unimolecular nature of these reactions. It is seen from Table VII that, when reduced amounts of *N*-chlorosulphamic acid are used, the superiority of chloride ions over nitrate ions for promoting the anti-shrink reaction with wool becomes more marked.

4. THE REACTION OF PHENOL WITH *N*-CHLOROUREA AND *N*-CHLOROSULPHAMIC ACID

The effects of different anions on the heterogeneous reaction between wool and *N*-chlorourea or *N*-chlorosulphamic acid having been determined, the effect of salts on the homogeneous chlorination of phenol by chloramines was investigated (Table VIII).

TABLE VIII

Reaction of Phenol with *N*-Chlorourea and *N*-Chlorosulphamic Acid

Salt added	pH of Soln.	Half-life (min.) $NHCl{\cdot}SO_3H$	$NHCl{\cdot}CO{\cdot}NH_2$
None ...	1·4	70	36
NaCl ...	1·4	0·5	0·5
KNO_3 ...	1·4	70	30
$Mg(ClO_4)_2$ ...	1·0	50	25
KF ...	5·3	∞	∞
Na naphthalene-β-sulphonate	1·1	35	22

When allowance is made for the effect of these salts on the pH of the reaction, it is seen that chloride ions are specific for promoting the chlorination of phenol by *N*-chlorourea or *N*-chlorosulphamic acid.

It should be borne in mind that, since the concentrations of chloramine and phenol are comparable[13], these reactions are of second order, whereas the reactions between chloramines and wool are of first order. Thus no comparison can be made between the rates of the reactions given in Table VIII and those of reactions with wool. It was found, for example, that *N*-chlorourea reacted with a large excess of phenol (ratio of phenol to available chlorine 50 : 1) in solution of pH 1·5 at 40°C. with a half-life of only 1·5 min. Under these conditions the reaction was of first order with respect to chloramine concentration.

5. EFFECT OF NITRATE IONS IN ACID SOLUTION ON WOOL

It is seen from Tables VI and VIII that salts which lower the pH of a 0·50% (wt./vol.) solution of sulphuric acid promote both the anti-shrink action between *N*-chlorosulphamic acid and wool and the rate of chlorination of phenol by *N*-chlorosulphamic acid or *N*-chlorourea. The effect of these anions on both reactions is quite small compared with that of chloride ions, and can be explained as a pH effect. The influence of nitrate ions on the chlorosulphamic acid anti-shrink reaction is difficult to understand. Although not as great as that of chloride ions, the effect of nitrate ions is quite marked (Table VII). These ions neither decrease the pH of sulphuric acid solutions nor promote the chlorination of phenol by chloramines.

In order to test the possibility that nitrate ions themselves exert an anti-felting action on wool, their action on wool patterns was examined (Table IX). All treatments were performed in 0·50% (wt./vol.) sulphuric acid solution at 40°C.

TABLE IX

Effect of Potassium Nitrate on Shrinkage of Wool Patterns

Treatment	Area Shrinkage (%)
(1) None	30·0
(2) *N*-Chlorosulphamic acid, no NaCl ...	20·7
(3) *N*-Chlorosulphamic acid + 10·0% NaCl in soln.	0
(4) *N*-Chlorosulphamic acid + 10·0% KNO_3 in soln.	11·2
(5) 10·0% KNO_3 + 0·50% H_2SO_4 soln. for 1 hr.	31·1
(6) (2) followed by (5)	23·2

It must be concluded, therefore, that the effect of nitrate ions is to influence the reactivity of *N*-chlorosulphamic acid itself, and is not due to their ability to exert an anti-felting action on wool.

6. CHLORINE CONTENT OF WOOL AFTER REACTION WITH *N*-CHLOROSULPHAMIC ACID

In Table X are shown the amounts of combined chlorine in wool after different treatments. These were performed in 0·50% (wt./vol.) sulphuric acid solution at 40°C., except the acid chlorinations, which were performed at 18°C. The treatment in acid sodium chloride solution alone was performed to enable the analytical results for the wool treated with *N*-chlorosulphamic acid in the presence of chloride ions to be corrected for chloride ions which remained in the wool after Soxhlet extraction.

TABLE X

Combined Chlorine in Wool after Treatment with *N*-Chlorosulphamic Acid

Treatment	Chlorine Content of Wool (%)	Mean
10·0% available Cl_2	0·67 0·36	0·52
10·0% Cl_2, as $NHCl{\cdot}SO_3H$, in 10·0% NaCl soln.	0·67 0·57	0·48*
10·0% Cl_2, as $NHCl{\cdot}SO_3H$, no NaCl	0·106 0·062	0·08
10·0% NaCl + 0·50% H_2SO_4 soln. for 1 hr.	0·18 0·11	—

* Corrected for 0·14% sorbed chloride ions

7. ENERGY OF ACTIVATION OF THE REACTION BETWEEN WOOL AND CHLOROUREA

The apparent activation energy of the reaction between wool and *N*-chlorourea in the presence of chloride ions, calculated from the velocity constants determined at two different temperatures, was found to be 8·5 kcal./mole, compared with the value of 12·7 kcal./mole previously found for the reaction with *N*-chlorosulphamic acid [12]. The reaction was also independent of the rate of stirring over the range 100–400 r.p.m., as is the corresponding reaction with *N*-chlorosulphamic acid.

8. PRODUCTS OF REACTION OF WOOL WITH *N*-CHLOROUREA AND *N*-CHLOROSULPHAMIC ACID

Although it seemed very probable that after reaction with wool *N*-chlorourea and *N*-chlorosulphamic acid would be converted to urea and sulphamic acid respectively, it was desirable to confirm this. Isolation of the end-products of the reactions from the large quantity of sodium chloride present (10·0% in solution) proved unsatisfactory, but the presence of these two substances was demonstrated as follows—

(*a*) After reaction of *N*-chlorourea with wool, an aliquot portion of the exhausted bath was treated with sodium hypobromite in a Lunge nitrometer. The nitrogen evolved corresponded to an 80% conversion of *N*-chlorourea to urea.

(*b*) After the bath of *N*-chlorosulphamic acid had exhausted on to the wool, the pattern was removed and sodium hypochlorite solution, equivalent to 4·0% available chlorine on the weight of the pattern treated, was added to the solution. Little odour of free chlorine was produced, and a further pattern of wool treated with this solution reacted with the same half-life as the original *N*-chlorosulphamic acid solution, viz. 10 min. The bath was regenerated four times in all, and in each case the solution reacted with fresh wool patterns with a half-life of 10 min. Since chlorine in acid solution reacts with wool at twice this rate, there can be little doubt that the exhausted bath contained sulphamic acid in an amount corresponding to the *N*-chlorosulphamic acid originally present.

Since the reaction of chloramines with wool is basically an oxidation and not a chlorination (see Table X), the overall reaction between wool and these chloramines must be represented as follows—

$$NH_2{\cdot}CO{\cdot}NHCl + W + H_2O \rightarrow NH_2{\cdot}CO{\cdot}NH_2 + WO + H^+ + Cl^- \quad \text{(i)}$$

$$NHCl{\cdot}SO_3H + W + H_2O \rightarrow NH_2{\cdot}SO_3H + WO + H^+ + Cl^- \quad \text{(ii)}$$

where W represents the structure of wool.

This does not preclude free chlorine from being the reacting species, as wool treated with chlorine itself contains little bound halogen. This is possibly due to hydrolysis of the initial reaction product between chlorine and the disulphide bond of the cystine residue.

Discussion

Kinetically, the reaction of wool with *N*-chlorourea differs from that with *N*-chlorosulphamic acid in a number of major respects. Thus, whereas the rate of reaction between *N*-chlorourea and wool is increased by chloride ions, the corresponding reaction with *N*-chlorosulphamic acid is retarded by these ions. Also the apparent activation energy of the reaction between *N*-chlorourea and wool is 8·5 kcal./mole, whereas that of the reaction with *N*-chlorosulphamic acid is 12·7 kcal./mole. In view of these differences the reactions between wool and the two chloramines are considered separately, as they cannot proceed by identical mechanisms.

THE REACTION OF *N*-CHLOROUREA WITH WOOL

The objections to the reaction between *N*-chlorourea and wool proceeding by reaction of the wool with the free chlorine present in the solution—

$$NH_2{\cdot}CO{\cdot}NHCl + H^+ + Cl^- \rightleftharpoons NH_2{\cdot}CO{\cdot}NH_2 + Cl_2$$

have been discussed in detail previously [12]. These conclusions are supported by the fact that solutions of chlorine of extremely low concentration still render fabric non-felting [14]. A solution of *N*-monochlorourea containing no chloride ions contains sufficient free chlorine to render fabric unshrinkable if the reaction were a simple chlorination.

An alternative and more probable mechanism for the reaction is one in which the *N*-chlorourea–chlorine equilibrium *within* the fibre is the important factor. Under these conditions *N*-chlorourea would diffuse into the fibre, where the equilibrium would be continuously disturbed by reaction of the free chlorine with the keratin, and urea would diffuse away from the fibre. Owing to the low concentration of free chlorine present [12], it is possible that reaction of this with the wool is very slow compared with the diffusion processes, and thus controls the overall reaction rate.

This mechanism is supported by two facts— (*a*) Wool treated with *N*-chlorourea, in either absence or presence of chloride ions, has an undisturbed scale structure, and the scales are not detached during milling [2]. This suggests that the reaction is not occurring on the surface of the fibres. (*b*) The experimental evidence is against these reactions being controlled by either a liquid or a solid diffusion process. Although the value for the energy of activation of the reaction is very near that of 8·0 kcal./mole found for the reaction between wool and potassium permanganate in

acid solution under conditions where the rate process is liquid diffusion[15], the independence of stirring of the *N*-chlorourea reaction must eliminate such a mechanism as the rate-controlling step. Also, if the reaction were controlled by diffusion through the fibre, then in the initial stages of the reaction it would be expected that a linear relationship should hold between $\sqrt{t}$ and x (x = amount of *N*-chlorourea which has reacted in time t)[16]. This did not occur, the reactions obeying the simple first-order law—

$$k = \frac{1}{t} \ln \frac{a}{a-x}$$

(a = initial concentration of *N*-chlorourea).

It must be noted, however, that the relationship between $\sqrt{t}$ and x is strictly true only for diffusion from a constant surface concentration into a semi-infinite solid, whereas under the experimental conditions used, diffusion within the fibre proceeds from an exhausting solution, i.e. a variable surface concentration. However, in the initial stages of these reactions the surface concentration is approximately constant.

It would appear that the rate-determining step is probably a true chemical reaction within the fibre, as opposed to diffusion through the liquid layer surrounding the fibre, or through the fibre itself.

The data given in Tables I, II, and IV lend themselves to quantitative treatment provided that three assumptions are made—

(1) The distribution of *N*-chlorourea between the fibre and the solution obeys the distribution law; i.e. the concentration in the fibre is directly proportional to that in solution, and is independent of other factors such as the chloride and hydrogen ion concentrations of the solution. Since *N*-chlorourea is a neutral molecule, this assumption is reasonable.

(2) The rate of attainment of the equilibrium—

$$NH_2{\cdot}CO{\cdot}NHCl + H^+ + Cl^- \rightleftharpoons NH_2{\cdot}CO{\cdot}NH_2 + Cl_2 \quad \text{(iii)}$$

is fast compared with the rate of reaction of the very low concentration of free chlorine produced with the wool.

(3) The concentrations of chloride and hydrogen ions which are produced within the fibre by reaction of the chlorine with the wool—

$$W + Cl_2 + H_2O \rightarrow WO + 2H^+ + 2Cl^-$$

are too small compared with the concentrations of these ions already present to influence the reaction.

In the equilibrium (iii), let the initial concentrations of *N*-chlorourea, hydrogen ions, and chloride ions be $[NH_2{\cdot}CO{\cdot}NHCl]$, $[H^+]$, and $[Cl^-]$ respectively, with the concentrations of urea and free chlorine both zero. If at equilibrium the concentration of free chlorine is $[Cl_2]$, then the equilibrium constant K_1 will be—

$$K_1 = \frac{[Cl_2]^2}{[NH_2{\cdot}CO{\cdot}NHCl]\,[H^+]\,[Cl^-]}$$

since $[Cl_2]$ is very small compared with the other concentrations[12] and $[Cl_2] = [NH_2{\cdot}CO{\cdot}NH_2]$. If the concentration of chloride ions is varied, the concentrations of *N*-chlorourea and hydrogen ions being kept constant, then—

$$K_2 = \frac{[Cl_2]^2}{[Cl^-]} \quad \text{or} \quad [Cl_2] = K_2\sqrt{[Cl^-]}$$

And since the rate of the reaction of the chlorine with the wool must be proportional to the concentration of chlorine produced by the equilibrium, then—

$$\frac{1}{t_{\frac{1}{2}}} = k\,[Cl_2] \quad \text{or} \quad t_{\frac{1}{2}}\,\sqrt{[Cl^-]} = \text{Constant}$$

where $t_{\frac{1}{2}}$ is the half-life of the reaction.

Similarly, it may be shown that the values of $t_{\frac{1}{2}}\,\sqrt{[H^+]}$ (at constant chloride ion concentration) and $t_{\frac{1}{2}}/[NH_2{\cdot}CO{\cdot}NH_2]$ (at constant chloride and hydrogen ion concentrations) will be constant. In the latter case $[Cl_2] \neq [NH_2{\cdot}CO{\cdot}NH_2]$ and the equilibrium constant must be written in the form—

$$K = \frac{[NH_2{\cdot}CO{\cdot}NH_2]\,[Cl_2]}{[NH_2{\cdot}CO{\cdot}NHCl]\,[H^+]\,[Cl^-]}$$

Although these deductions are in good agreement with the experimental data, this treatment must be regarded as only approximate, since equilibrium conditions alone have been considered. As the reaction with the wool proceeds, the value of $[NH_2{\cdot}CO{\cdot}NHCl]$ falls to virtually zero, while the value of $[NH_2{\cdot}CO{\cdot}NH_2]$ correspondingly increases, thus producing a large decrease in the concentration of free chlorine.

It should be emphasised, however, that the similarity of the effect of either hydrogen or chloride ions on the reaction, i.e. that $t_{\frac{1}{2}}\,\sqrt{[Cl^-]}$ and $t_{\frac{1}{2}}\sqrt{[H^+]}$ are both constants, in itself is good evidence for the mechanism proposed.

THE REACTION OF *N*-CHLOROSULPHAMIC ACID WITH WOOL

In view of the fact that wool after reaction with *N*-chlorosulphamic acid in the absence of chloride ions contains only 0·1% combined chlorine, whereas wool treated with an equivalent quantity of free chlorine contains 0·5% (Table X), it seems probable that the reacting species in the former reaction is not chlorine. The overall reaction as given by equation (ii), which does not involve free chlorine, may denote the actual reaction mechanism.

The general retardation of the reaction between *N*-chlorosulphamic acid and wool by anions (Tables III, VI, and VII) is consistent with the reaction proceeding by an ion-exchange mechanism.

If wool is immersed in a solution containing *N*-chlorosulphamic acid and another strong acid HX, i.e. the experimental conditions under which wool has been treated in this work, the following will take place. The ionised carboxyl groups of the wool, $-COO^-$, will combine with protons, and to restore neutrality $NHCl{\cdot}SO_3^-$ and X^- anions will be associated with the fibre as gegenions, when the following equilibrium will be set up—

$$NHCl{\cdot}SO_3^-{}_{\text{fibre}} + X^-{}_{\text{soln}} \rightleftharpoons X^-{}_{\text{fibre}} + NHCl{\cdot}SO_3^-{}_{\text{soln}}$$

The addition of further anions X^- to the solution must increase the value of X^-_{fibre}, and since—

$$NHCl{\cdot}SO_3^-{}_{\text{fibre}} + X^-{}_{\text{fibre}} = A$$

(A = acid-combining power of wool = 88 milli-equiv./100 g.), the value of $NHCl{\cdot}SO_3^-{}_{\text{fibre}}$ will be

reduced. This must produce a decrease in the rate of the reaction between the *N*-chlorosulphamic acid and the wool.

This concept of *N*-chlorosulphamic anions having to compete with other anions to gain access to the wool fibre explains the effect of salts on the reaction, at least qualitatively. Quantitatively, this mechanism is supported by the energy of activation of the reaction of 12·7 kcal./mole, since the exchange of anions on wool fibres requires activation energies of 10–14 kcal./mole [17]. Although the values of $t_{\frac{1}{2}}$ for these reactions are rather large for such a process, it is possible that reaction of the *N*-chlorosulphamic acid with the wool occurs only at specific sites.

Recently Hudson has determined the rates of reaction of a number of acids with wool [18]. The rates for different acids bear the same relationship to one another as do the rates of the reactions between *N*-chlorosulphamic acid and wool in the presence of the corresponding anions, and are compared in Table XI.

TABLE XI

Comparison of Acid Absorption on Wool with Effect of Anions on the Reaction between *N*-Chlorosulphamic Acid and Wool

Reaction of Wool with Acid HX at 19°C.		Reaction of Wool with *N*-Chlorosulphamic Acid in Presence of Anions at 40°C.	
Anion X^-	$t_{\frac{1}{2}}$ (min).	Anion (0·50 M.)	$t_{\frac{1}{2}}$ (min.)
NO_3	1·8	NO_3	18
$C_6H_5{\cdot}SO_3$	4·3	$C_6H_3(CH_3)_2{\cdot}SO_3$	50
$C_{10}H_7{\cdot}SO_3$	6·5	$C_{10}H_7{\cdot}SO_3$	60

The significance of the similarity of these results may be that, whereas in acid absorption the larger anions enter the wool fibre more slowly, in the reactions with *N*-chlorosulphamic acid they leave the fibre more slowly and retard the ion exchange to a similar degree.

Alternatively, since larger anions have a greater affinity for wool [19], the concentration of the chlorosulphamic acid anion within the fibre will be reduced when these anions are present, and hence the rate of reaction of the chlorosulphamic acid will be slower. Either explanation is in keeping with an ion-exchange mechanism for these reactions, but the quantitative correlation between the results compared in Table XI suggests that the rate of diffusion of the anions is probably the more important factor.

Although the effect of chloride ions on the promotion of the anti-shrink reaction may be the same as that occurring in the reaction with *N*-chlorourea, and may be due to the production of chlorine within the fibre—

$$NHCl{\cdot}SO_3H + H^+ + Cl^- \rightleftharpoons NH_2{\cdot}SO_3H + Cl_2$$

this does not account for the effect of nitrate ions on the reaction. No explanation for the latter can be advanced.

II—Reactions between Wool and *N*-Bromamines

DISCUSSION

This discussion is based on previously published data on reactions between wool and *N*-bromoacetamide $CH_3{\cdot}CO{\cdot}NHBr$ and *N*-bromosuccinimide [3] $({\cdot}CH_2{\cdot}CO)_2NBr$.

Whereas the concentrations of free chlorine in reactions between chloramines and wool are so low (ca. 5×10^{-6} mole/litre) that they cannot be used as criteria to determine whether free chlorine has played a major part in the reactions [13], the concentrations of bromine in the corresponding reactions with *N*-bromoacetamide and *N*-bromosuccinimide show that these reactions are partly, at least, brominations. Thus the concentration of free bromine, which is virtually zero at the beginning of these reactions, rises to a maximum of ca. 10^{-3} mole/litre, which corresponds to 20% of the total oxidising power originally present.

The difference in the free halogen concentrations present in the reactions is due to the fact that in the case of the chloramines discussed in Section I the equilibrium—

$$AX + H^+ + X^- \rightleftharpoons AH + X_2$$

(X = Cl or Br) lies nearly completely on the halogenoamine side, while with the bromamines it lies nearly completely on the free halogen side.

Two difficulties arise if it be postulated that the reactions between *N*-bromoacetamide or *N*-bromosuccinimide and wool proceed exclusively via free bromine—

(1) The reaction solution initially is free from bromine and bromide ions, and yet one of these is essential to initiate the following chain mechanism—

$$W + H_2O + Br_2 \rightarrow WO + 2H^+ + 2Br^- \quad \text{(i)}$$

$$ABr + H^+ + Br^- \rightleftharpoons AH + Br_2 \quad \text{(ii)}$$

(2) A large excess of succinimide fails to retard to a significant degree the reaction between *N*-bromosuccinimide and wool, although the corresponding reaction with *N*-bromoacetamide is slowed down by an excess of acetamide, as would be expected if the reaction were a simple bromination.

Although the assumption that bromamines may undergo direct reaction with wool—

$$W + ABr + H_2O \rightarrow WO + AH + H^+ + Br^- \quad \text{(iii)}$$

resolves both difficulties, alternative explanations are possible.

These reactions could be initiated by hydrolysis of the bromamine to a small quantity of hypobromous acid—

$$ABr + H_2O \rightleftharpoons AH + HOBr \quad \text{(iv)}$$

which was not detected by the photometer used in the analysis of these solutions. The hypobromous acid could then oxidise the wool with the formation of bromide ions—

$$W + HOBr \rightarrow WO + H^+ + Br^- \quad \text{(v)}$$

which would initiate reactions (i) and (ii).

It is important to note that, whereas in the case of the chloramine reactions it is reasonable to ignore the chloride ions eliminated from the wool

after reaction (p. 94), as their quantity is negligible compared with that of the chloride ions in solution, in the reactions under discussion this is clearly not so. All the bromide ions in the system initially are associated with the wool, and thus the concentration of free bromine within the fibre must be considerably greater than that in solution. Under these conditions, although an excess of succinimide will suppress the free bromine in solution, that within the fibre will not be reduced to a corresponding extent—

$$(\cdot CH_2\cdot CO)_2NH + Br_2 \rightleftharpoons (\cdot CH_2\cdot CO)_2NBr + H^+ + Br^-$$

Kinetically, reactions between bromamines and wool are more complex than reactions between wool and chloramines. Whereas the latter are of first order throughout the reaction, the bromamine reactions are of first order until the half-life is reached, after which the value of k increases rapidly. The energy of activation E_{0-20} calculated from the initial values of k is 6·6 kcal. per mole [20].

The increase in the value of k as the reaction proceeds is in accordance with the mechanism given by equations (i) and (ii), but its constant value in the initial stages of the reaction suggests that a diffusion mechanism, involving the bromamine itself, is probably the rate-determining factor. The energy of activation points to this being a liquid diffusion process.

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EXPLANATORY PAPER ON MODERN THEORY

Theories of Dyeing

II—Dyeing Processes in Action

H. A. TURNER

So seh' ich in allen
Die ewige Zier.
GOETHE

GENERAL

Our discussions in Part I[1] were concerned with completed dyeing processes, carried to the point of equilibrium beyond which no further effect is to be expected unless, during the dyeing, we have succeeded in making some change in the fibre or the dye. It would, however, not be far from the truth to say that some 60 or 70% of the practical problems of dyeing occur while the dye is actually going on. With substantive dyes, applied by the conventional methods, the rate of uptake is greatest in the early stages of dyeing, and is thus hardest to control. The more accurate our knowledge of the course of the dyeing processes at these early stages, the greater the chances of a real increase in the efficiency of the technical procedures. Practically, the whole secret of obtaining levelness and penetration consists in making sure that the rate of adsorption of dye from solution by the fibre does not get in front of the regular and uniform mechanical distribution of that solution among all the textile fibres which make up the yarn or fabric which is being dyed. The kinetic study of dyeing is therefore at least as important as the static study which has claimed our attention in Part I[1]. Indeed, for the worker who is carrying out experimental measurements under refined laboratory conditions, the data which concern equilibrium conditions are by-products of more extended determinations which follow the course of the dyeing from its initiation. It has been repeatedly stated that one of the advantages of the thermodynamic approach is that, on the whole, it introduces simplicity into complicated phenomena by concentrating on the beginning and the end of changes, and ignoring as far as possible the intermediate details. This mental attitude cannot, however, be carried too far, because some of the details which it is convenient to ignore in the first place may be very important.

RATE-OF-DYEING CURVES

Practically all the information required for the development of the subject comes from rate-of-dyeing experiments. These experiments are small-

scale, carefully controlled replicas of the technical dyeing processes. A known weight of carefully selected, fully representative, purified textile material is introduced into a dyebath of known composition and known volume, and great care is taken that no change in the volume of this bath, from either evaporation or other cause, takes place during the whole course of the experiment. Immediate wetting must occur, the temperature of the bath must not fluctuate by more than about 0·1°c. during the experiment, and circulation of the liquor relative to the textile material must be constant and uniform. Stirring or mechanical reciprocation of the sample is the favourite means of achieving the last requirement, although, in one apparatus at least, the liquor is circulated through the sample by means of a small pump. Measurement of the time of dyeing starts from the introduction of the sample. After a carefully measured time, it is necessary to find out how much dye has left the solution and has been taken up by the fibre. Wherever possible it is arranged that the measurement of quantities or concentrations of dyes shall be through the light-absorbing power of their solutions, that is with a colorimeter. Since the photoelectric cell has been perfected as a substitute for the human eye, these measurements have become increasingly convenient and rapid. Two alternatives face the worker. He can measure the weakening of colour in the dyebath, perhaps without disturbing the experiment at all. This way is convenient, but may not be sufficiently accurate. Generally, the dyed sample is taken out, freed from the adhering dye liquor, and then stripped with a solvent which extracts all the dye from it. The amount of dye in the extract is then determined. The dye uptake is plotted along one axis of a graph and the time along the other. Thus, at least one experiment is necessary for each point on the curve.

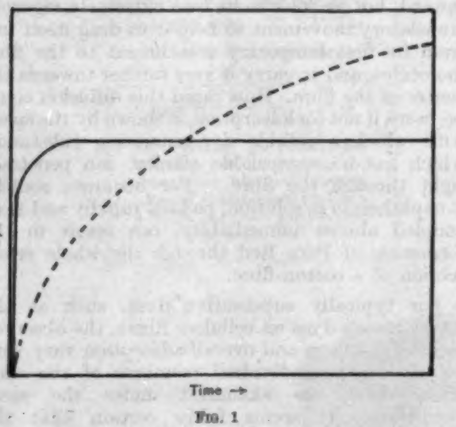


FIG. 1

Fig. 1 is an example of the kind of result that may be obtained. It shows an initial rapid take-up of the dye in the early stages, the take-up getting less and less in successive equal time intervals until the curve ceases to rise any more, showing that dye absorption has ceased. In Fig. 1 two curves have been drawn, the unbroken curve representing the dyeing behaviour of one dye and the dotted curve that of another. The curve for the first dye rises more rapidly at the beginning than that for the second, and so the first dye would be called the more rapidly dyeing of the two. As often happens, it flattens out at a lower value of dye take-up than the second, and this means that the more slowly dyeing dye, if it is given sufficient time, will exhaust more completely. As would be expected from their practical behaviour, the dyes produce different curves as the dyeing conditions (initial concentration of dye, concentration of assistant present, temperature, kind of fibre, etc.) are altered, and practically the whole of the dyeing properties of any given dye can be summarised in a series of curves of this kind. Records for a large number of direct dyes have been prepared, for instance, by the Geigy Company in such a form that the information is readily available for use in deciding the practical conditions under which the single dyes should be used.

The physical chemist, however, requires more from the curves than this. We have seen that dyeing starts fast and slows down to an ultimate standstill. The rate or speed of the process is changing all the time. If we are asked what is the rate of dyeing of, say, Chrysophenine G on bleached cotton, with all the dyeing conditions specified, we shall have to ask: "How long after the start?". It may be that, with all the conditions the same, Chlorazol Brown M is being adsorbed more rapidly than Chrysophenine G at the end of the first ten minutes, but the order will probably be reversed at the end of an hour. We want first the means of finding the speed of dyeing at any time during the operation, and from this to get a number which can represent the inherent capacity for rapid adsorption freed from all accidental conditions, in very much the same way as the fundamental value for affinity was arrived at.

RATE OF DYEING

The investigator will need to be able to determine how fast dyeing is proceeding at any time during its course, in terms, say, of milligrams of dye taken

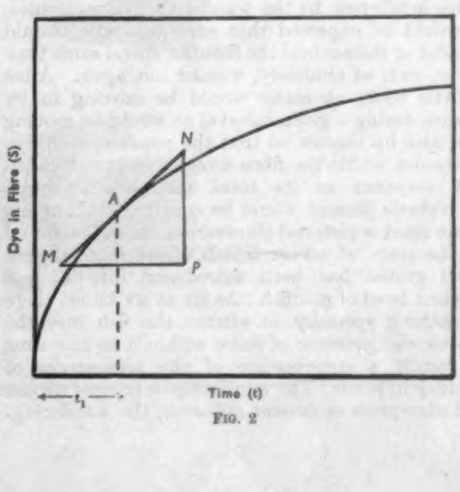


FIG. 2

up per second. We would expect this figure to be elusive, since its value changes continuously. There are means of calculating it based upon the use of the differential calculus, and these will be the more accurate, but a quite reasonable figure can be got from the rate-of-dyeing curve, as shown in Fig. 2. Let us take a point A on the curve, corresponding to the time for which we need the information. We draw a line through this point so that it just grazes the curve, but does not cut it. This is the tangent. The gradient or slope of this tangent represents the rate of dyeing for the conditions at A. Somewhere along the length of the tangent we draw a horizontal line which cuts it at M, and a little to one side we draw a vertical line cutting the tangent at N and the horizontal line at P. We measure PN and from the scale of our graph find how many milligrams of dye it represents. Similarly, we measure the line MP, and from the graph find how many seconds it represents. Dividing the first quantity by the second gives the rate of dye uptake at the instant when dyeing has been going on for just t_1 seconds. Without fully understanding how it has been got, or what it would mean to a mathematician, let us take the symbolism of the calculus for the value we have just found and represent the rate of dyeing by $\mathrm{d}S/\mathrm{d}t$. We shall probably be able to fit this quantity into its place later.

DIFFUSION AND DIFFUSION COEFFICIENTS

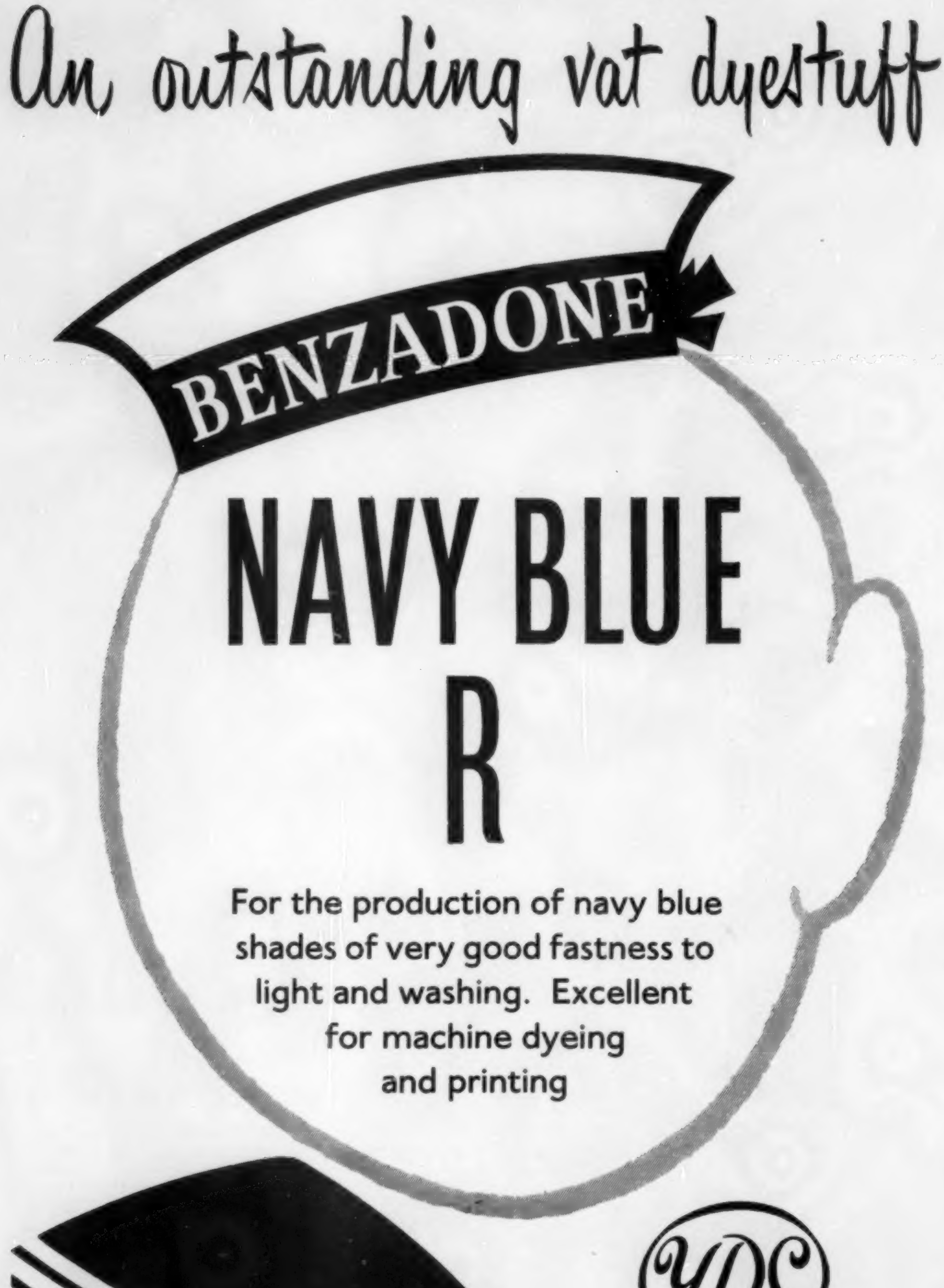
Before any further progress can be made, and we can go on to obtain a figure which can represent the general alacrity with which a dye can pass from its solutions in the bath to the inside of the fibre, we must form a picture of what is happening. When an undyed fibre is put into the bath, its accessible pores and fissures rapidly fill with water molecules and so are opened up for the entry of dye molecules. The dye molecules in solutions are wandering about in aimless motion, more or less crowded according to the concentration at which the solution was made up. We have already seen in Part I[1] that, as new space, here represented by the pores of the fibre, is made available, molecules will move into it from the more crowded spaces in the solution. If the walls of these fissures were quite indifferent to the wandering dye molecules, it would be expected that such molecules would wander or diffuse into the fissures, spend some time there, and, as aimlessly, wander out again. After a little time, as many would be moving in by chance during a given interval as would be moving out, also by chance, so that the population of dye molecules within the fibre would remain substantially constant in its total numbers, although individuals present would be constantly changing. If we need a pictorial illustration, it can be found in the state of affairs which exists soon after a coral grotto has been introduced into a well stocked bowl of goldfish. As far as we know, there is nothing specially to attract the fish into the grotto: the presence of some within it at any time is merely a consequence of the aimlessness of goldfish in bowls. The wandering-in process we can call *absorption* or *inward diffusion*; the wandering-out, *desorption* or *outward diffusion*; the balance of the two processes represents equilibrium.

When dealing with fibres, the analogy given above might be translated by representing the goldfish by the molecules of some chemically inert gas such as argon, but with dyeing there is nothing quite so simple. It has been the main theme of much of Part I[1] that there is a definite linkage by chemical forces between the molecules of dye and those which compose the fibre. Thus, once the dye is in the fibre, the freedom to get out again is strictly limited. The system has been weighted: someone has been putting ant-eggs in the grotto. In other words, diffusion is accompanied by *adsorption*. In few examples of dyeing is the attachment of dye to the fibre absolute, or completely incapable of reversal. If this were not so, we should have 100% exhaustions and complete fastness to washing. Some dye molecules do manage to break away and diffuse out of the fibre again. This fact may be a source of assistance to the dyer in helping him to correct initially unlevel dyeings.

Common sense suggests what more minute examination reveals to be true about the manner in which dye finds its way from the dyebath to the centre of the fibre during the dyeing process. A grosser analogy, frequent in the experience of the practical dyer, is given by the dyeing of a tightly twisted yarn with a substantive dye. In the early stages of the process, dye is captured from the solution so rapidly that the dyed portion of the yarn is no more than a thin peripheral zone. On this scale of operations, there is sometimes hope of attaining a more uniform distribution across the diameter of the thread by mechanical intervention, i.e. by moving the dyebath so quickly that a supply is carried into the thread before the solution can be denuded by adsorption. On the small scale, at molecular magnitudes, the dye cannot be carried inward, but we look to its own extremely vigorous translatory movement to help it to drag itself free from its first temporary attachment to the fibre molecules, and to carry it ever further towards the centre of the fibre. How rapid this diffusion could be, were it not for adsorption, is shown by the speed with which a soluble dye-generating substance, which has no appreciable affinity, can penetrate right through the fibre. For instance, sodium β-naphtholate in solution, padded rapidly and then coupled almost immediately, can result in the formation of Para Red through the whole cross-section of a cotton fibre.

For typically substantive dyes, such as the direct cotton dyes on cellulose fibres, the observed rates of diffusion and overall adsorption vary very greatly among individual members of the class when these are examined under the same conditions. It seems fairly certain that the technical application of these and similar dyes cannot be under efficient control until more is known about the actual mechanism of the processes which take the dye from the outside to the inside of the fibre. To carry out direct measurements of the movement of dye from point to point in the fibre, like the timing of a motor-cycle race


HANNA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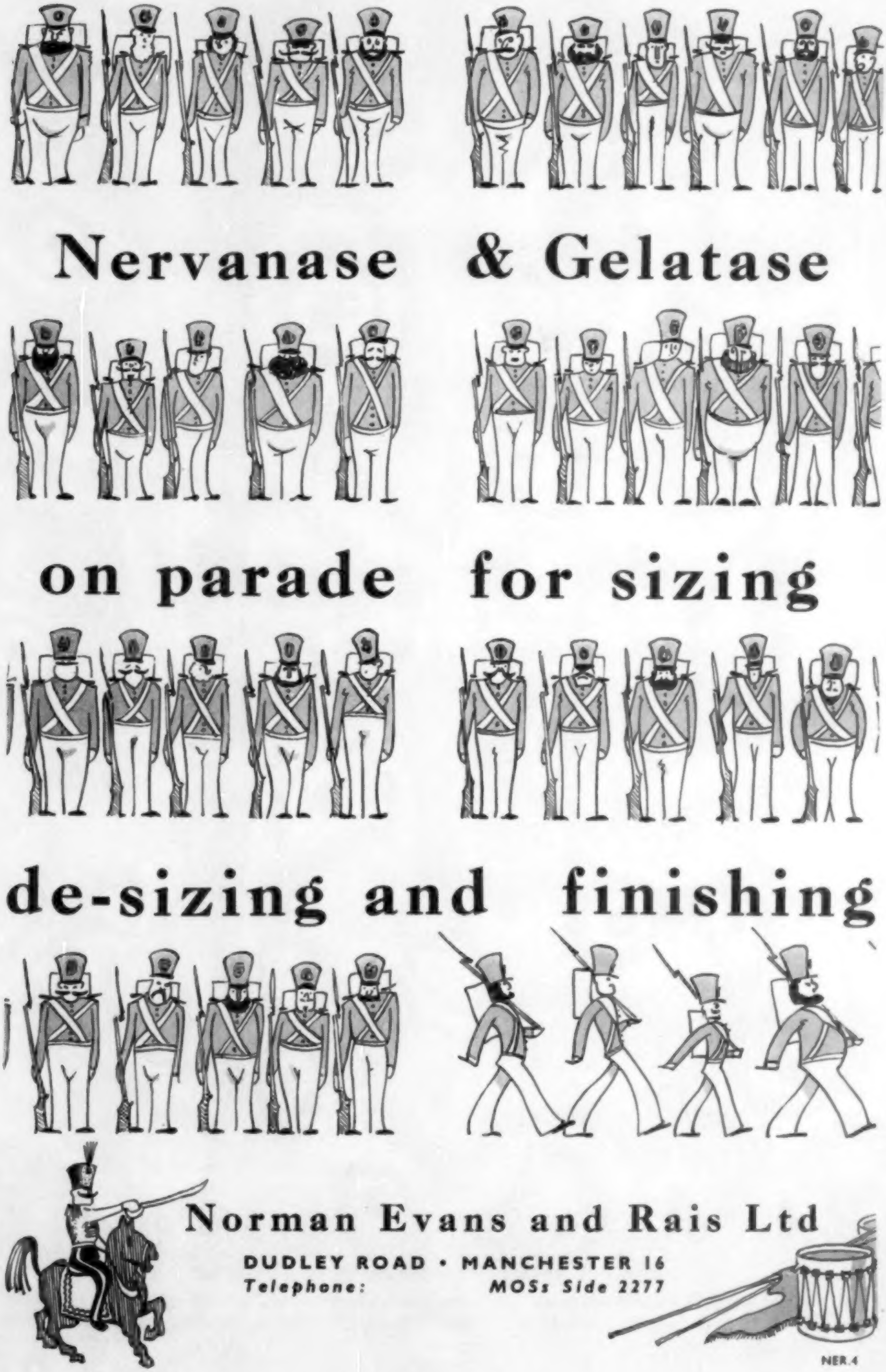
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lap by lap, is not beyond experimental possibility, but it is certainly extremely difficult and laborious. Consequently, attempts have had to be made to deduce the progress of the dye into the fibre from the data of the rate-of-dyeing curves, which tell only of the overall distribution of dye between solution and fibre at any given time, and cannot say anything about the local details at points within the fibre. For this combined process of measurement and deduction to be carried out successfully, it is necessary to suppose a likely dyeing mechanism, and then to see whether, by its aid, we can construct rate-of-dyeing curves which agree reasonably well with those furnished by actual experiment.

This kind of approach has dominated a great deal of the work which has been done on the kinetic or "moving" aspects of the dyeing processes. A theoretical prediction has been made, checked by experiment, and found to be substantially true but with important discrepancies; the theory has been amplified in such a way that these discrepancies vanish. And so the routine has gone on.

The investigators have been helped by knowing that, although the secondary details may be very distinctive, the dyeing processes are fundamentally similar to many other phenomena in which a gas or a dissolved substance is taken up intimately between the constituent molecules of a solid body. They are, in fact, all examples of what the physical chemist calls *adsorption*. Mechanisms which have been worked out for other systems, where the theoretical development seems less obscure, can be "tried for size" upon dyeing phenomena before the distinctive needs of these phenomena are catered for. Thus, when a particular mathematical treatment was needed to describe the passage of direct dyes into cellulose foils and fibres, it was found almost ready-made in some abstract speculations of the physical chemist McBain, which had been adapted to describe the passage of oxygen into muscle tissue by the biophysicist A. V. Hill.

Let us therefore take all the directly measurable data about the dyeing of, say, a cellulosic fibre with a direct cotton dye, and then see at what point it is necessary to leave the operations of direct observation and begin those of deduction. The best way to outline the course of the process would be to dye different samples of the fibre for different times and then to see how penetration of the dye has progressed by cutting thin sections at right-angles to the length and looking at them with the microscope. In the early stages, more or less pronounced ring-dyeing will be seen; i.e. there will be more or less intense coloration in a very thin ring at the outer edge of the section, with the centre empty of colour. As time goes on, the ring thickens with a shaded inner edge, until at last there is some colour in the whole area of the section, but fainter in the centre than at the rim.

At all these stages there have existed what are called *concentration gradients*, which are capable of accurate numerical definition. A line is drawn from the outside of the fibre section to its centre. This is divided up into small equal lengths, and with each of these lengths as a side small squares are drawn resting on the line. The dye in the different small areas is determined, representing the local concentrations at various stages from the outside to the centre. Suppose it is found to be two-thousandths of a milligram in one square and one-thousandth of a milligram in the next square as we move towards the centre. Then the concentration difference between the two unit squares is one-thousandth of a milligram of dye. Suppose that we have made each of these small areas to have a side of one-thousandth of a millimetre. Then in moving this distance into the fibre, the concentration has diminished by one-thousandth of a milligram. The concentration gradient could be expressed as (1/1000) unit of concentration divided by (1/1000) unit of distance, or unity. It would be given a negative value, i.e. -1, because we have found the concentration to *decrease* in the direction in which we have been measuring. Again following the same practice as was used for expressing rate of dyeing, i.e. change of dye present with time, we will express change of concentration with distance by $\mathrm{d}C/\mathrm{d}x$ and say that $\mathrm{d}C/\mathrm{d}x = -1$.

This equation is not an artificial mathematical abstraction but has a very real and important technical meaning. Many times we have seen that one of the most important influences in making dye go from place A to place B is that it is more crowded in A and there is more room for it in B. The concentration gradient is a precise statement of the incentive for the dye in the fibre to move. In the first little square area there was a certain crowding or concentration. The second little area was not completely empty, but there was less dye, and therefore more room, in it than in the first. Consequently the incentive towards movement in those parts of the fibre was the difference in concentration between the two areas. By taking very small portions of the total cross-section, we were able to pinpoint the state of affairs in one very small region of the fibre, and by carrying out similar measurements at other places it is possible to see how the incentive towards movement stands at any particular place at any particular time.

Ultimately, if dyeing goes on for a long time, the fibre becomes evenly dyed from rim to centre (or so it is convenient to believe, for this is a point which refinement in the technique of examination may show to be not quite true). Then the concentration in any two adjacent areas will be the same, the difference in concentration between the two will be zero, the concentration gradient will be zero also, and the incentive towards any further movement of dye will disappear.

FICK'S LAW

All the above considerations have been epitomised in a very simple scientific rule for diffusion which goes under the name of Fick's law. It is that the rate of passage (diffusion) of a substance at any point in a system is proportional to the concentration gradient (incentive to movement) at that point. In the symbolic expression—

$$-\frac{\mathrm{d}S}{\mathrm{d}t} = D \times \frac{\mathrm{d}C}{\mathrm{d}x} \qquad \text{(i)}$$

The negative sign is only an expression of the way round that the system is viewed, i.e. that the dye will tend to go from a place of high to a place of low concentration. In the very simplest applications of the law, the factor which has been represented by D will have a constant value for a particular system, for a particular dye in a particular fibre. Because diffusion is influenced by the physical structure of the medium through which movement is taking place— for we should expect a dye to move faster in a fibre in which the molecules were relatively loosely packed, e.g. viscose rayon, than in one where the packing is much tighter, e.g. cotton— the fibre must be specified very closely. It is of no use specifying the fibre-substance as cellulose, and leaving it at that, as was done in calculating the affinity of dyes. Similarly, dyes are expected, and are known, to differ in their specific rates of diffusion. Those with small molecules might be expected to move faster under the influence of a given incentive. Those which are strongly attracted to the molecules of the fibre-substance may be expected to move more slowly, irrespective of their size. These do in fact form important questions for investigation.

Given this difference among different dyes, it would be very convenient to be able to compare their readiness to diffuse. D is a means of doing this. It represents the standard diffusion behaviour or rate of diffusion under unit conditions which apply equally for any dye. It is called the *diffusion coefficient*.

MEASUREMENT OF DIFFUSION COEFFICIENTS

The imaginary process by which the derivation of Fick's law and the concepts of rate of diffusion, concentration gradient, and diffusion coefficient have been obtained is a perfectly feasible one, but experimentally it is extremely difficult. For it to be successful we should have to devise methods for looking at various places within a fibre while it was being dyed, and looking with such accuracy that we could express local concentrations within the fibre to a margin of error of a few per cent only. Even the examination of cross-sections, directly through the microscope or via photographs, is not too easy, and would give only very rough results. It would be necessary also to get specimens at very short time intervals in the early stages of dyeing, when dye uptake from the solution can be very fast. Consequently an attempt has been made to deduce the particulars of local dye distribution and movement within the fibre from rate-of-dyeing experiments which tell us only the temporary distribution of dye between the bath as a whole and the fibre as a whole. It is evident that a big jump is necessary in the reasoning at this stage. In Fick's law above, the local rate of movement dS/dt is restricted to a single instant of time and the local concentration gradient dC/dx to a very small part of the whole fibre. These values are called *differential coefficients* and the law is written in the form of a *differential equation*. The methods of the calculus are being used, as is necessary when systems are being examined which are on the move and are changing from place to place and from moment to moment. In this form, however, there is very little chance of getting at the truth by direct measurement. All our quantities are too elusive. We must follow what the mathematician and the physicist call a process of integration: we must let all these minute changes go on adding up for an appreciable time, we must let the diffusing dye molecules go a measurable distance, although their speed may have been changing all the time, and then find out what overall change has occurred. If we are lucky in our mathematics and imaginative in the view of what may be happening, we may find that the theoretically predicted total change is just about the same as the one that we have measured. Then we have some justification for thinking that our imagined mechanism is correct.

The process may be illustrated by an operation which spreads over miles instead of thousandths of a millimetre. Suppose observers are set to work over the main route between Manchester and Blackpool studying the way in which the motor traffic passes at various fixed points at different times, so that finally certain rules are worked out which connect traffic density with all the different conditions of the day and season. These would be equivalent to rules of the type of Fick's law. On the basis of these rules it may then be possible to calculate quite accurately, without actually being present, the number of cars that pass in one hour through Preston, knowing only those which leave Manchester and those which arrive at Blackpool. This is analogous to what Neale did in the early days of direct dyeing research, when, by employing A. V. Hill's method of integrating Fick's law, he was able to calculate rate-of-dying curves for Chlorazol Sky Blue FF which were very close to those which had been completely determined by experiment. This showed at least that the dyeing of cellulose with direct dyes must, in essence, be a process of diffusion, not far from the simple pattern that Fick had envisaged.

There were, however, as there always are when natural phenomena are investigated and analysed more closely, some deviations which the simple idea would not explain. It was soon realised that the basic diffusion properties of a given direct dye were not constant under all conditions; i.e. the value of D for the dye did not remain constant when certain important conditions were changed. One variation was expected, that which came from changing the temperature. D will change as the temperature changes, in the most straightforward examples reflecting a higher intrinsic diffusing power, because the dye molecules then move faster and cannot be delayed so much by the attraction of the fibre. But it was also found that the results could be explained only by assuming that the intrinsic "diffusibility" could and did change with the locality in a partly dyed fibre. Most experiments agree in showing that it increases with increase in the concentration of dye at a particular spot. Thus, apart from the effect of *differences* of concentration — the concentration gradients or incentives to diffusion— it seems that a dye molecule can move faster through a fibre when there are many other

dye molecules round it than when there are few. Finality, either in defining the phenomenon or in explaining it, has not yet been reached, but it is now accepted that the diffusion coefficient has a rather restricted meaning, and not a universal significance. To take this kind of variation into account makes any kind of calculation more difficult, and it is not easy to find any direct means of investigation. Neale tried to expand the model of a cellulose fibre into something much bigger, so that he could then take the whole to pieces after it had been dyed for a given time, to find out what had been happening in different places. He dyed a large number of Cellophane sheets when they were tightly clamped together in a pack, and then tried to find how the dye was distributed in consecutive sheets. The variability of the diffusion coefficient with the prevailing dye concentration was confirmed, but other distractions were met with, and so all the information that had been sought could not be obtained.

CONCENTRATION AND POTENTIAL BARRIERS

The names, given in this heading to certain well defined effects which influence the course of dyeing for many fibres, but which were first looked into thoroughly for the dyeing of the direct cotton dyes on cellulose, are, to say the least, scientifically colloquial, and belong to the same class of terms as "sonic barrier", which is now so topical. Neale again must take a large share of the credit for starting investigation and speculation. He was led to think about them partly because of the evidence, mentioned above, that the diffusion coefficient does not remain constant when the concentration changes, and, perhaps more fundamentally, by the desire to find out why the addition of salt to the dyebath increases the uptake of dye. The latter effect can be demonstrated very graphically with pure specimens of certain direct dyes. This was first shown many years ago by Knecht, and later was fully confirmed by Neale. One of the classic observations of Neale was that, if pure Chlorazol Sky Blue FF is dyed from dilute dyebaths with all salt excluded, the dye has no substantivity. It will be found that the effect of salt can be predicted by substituting the increased concentration of sodium ions, resulting from the addition of sodium chloride, in the thermodynamic equations that have been put forward in Part I[1] for the calculation of affinity. This is, however, a much later development, and Neale's conclusions were reached by much less sweeping stages, although here, also, thermodynamic concepts play their part in the argument.

To show what the salt is thought to do, it is necessary to go back to some of the intimate pictures that have been drawn of the mechanism of substantive dyeing. Chlorazol Sky Blue FF exists in solution, as we have seen, as a negatively charged dye ion with four positively charged sodium ions within the range of electrical attraction. These four must always be within reach of the dye ion: ions cannot normally exist in a solution without sufficient oppositely charged ions to keep the whole electrically neutral. It does not follow, however, that the dye ion will always be accompanied by the same four sodium ions: sometimes one of them will move out of range, but only as another from somewhere else in the solution is able to move in and take its place. Cellulose is put into the solution, and as the dye ions come into contact with it during their wanderings they become attached to the accessible molecules of the fibre through hydrogen bonds. For each dye ion so captured, the complementary sodium ions must remain in the vicinity, although they are not directly capable of attachment to cellulose. Thus if there is crowding of dye ions at the surface of the fibre, the crowding of sodium ions is very much greater. These sodium ions, being small and lively, tend to go back into the dyebath, where there is much more room for them, but they cannot do so alone; they must detach the dye ion from the fibre and take it with them, for the two different types of ion are, as we have seen, bound together by electrical attractions. Before the building-up and crowding of dye at the surface of the cellulose has gone very far, this is precisely what happens, either the sodium ions dragging off the dye that has already been adsorbed or else those in the solution preventing more dye from going on. This state of affairs is established soon after the dyeing has begun, and before more than an extremely thin layer of dye has formed at the surface of the fibre. Thus the exhaustion which can be obtained is negligibly small, and no dyeing in a practical sense can be detected.

What happens when salt is added to the bath? Sodium chloride or sodium sulphate will bring in more sodium ions, and because the molecular weights of these salts are so much smaller than that of the dye, the introduction of moderate proportions of salt increases the crowding of the sodium ions in the bath very greatly. The crowding effect is even greater than is implied by the simple rise in concentration. It was seen earlier that, in so far as the effect on the dyeing of Sky Blue FF is concerned, the effective crowding factor for the sodium ion is given by the concentration multiplied by itself four times, since four is the valency of the particular dye ion. The bath being now so much more crowded with the sodium ions, there is no longer the incentive for them to diffuse from the vicinity of the fibre, and therefore the adsorption of the dye ions is neither reversed nor inhibited. This state of affairs comes about because dye ions in the fibre are the centre of two kinds of attractions, towards the fibre itself through the non-ionic hydrogen bonds and towards the sodium ions through electrovalencies. The behaviour of systems in which this kind of mechanism is operating is defined quantitatively by a principle called the *Donnan membrane equilibrium*, from the name of the physical chemist who first enunciated it. It can be seen in action in many systems when certain ions are taken up selectively by solid bodies from solution. Donnan himself first investigated it by using the dye Congo Red, and Neale was one of the first to use it to explain the dyeing of cellulose and also to show how the sodium and

hydroxyl ions are distributed between the lye and the cotton during the mercerisation process.

This superficial region highly crowded with molecules, which discourages the entry of more dye into the fibre, can be regarded figuratively as a material obstacle or barrier.

Connected with this effect, but most simply considered by itself, is the phenomenon of the *potential barrier*. This may always be set up when the dye comes to the fibre from the dyebath as a coloured ion, i.e. as an electrically charged particle. Practically all the substantive ionisable dyes for cellulose give rise to negatively charged dye ions, and it is easier to restrict consideration to this fibre-substance and to this type of ion. With protein fibres the possibilities are extended, but no change in principle is introduced. To start at the true beginning, the story should deal first with the dyeing of, say, viscose rayon with a highly purified direct dye— Sky Blue FF is a good example, not necessarily because it has become fashionable for the investigator in this field, but because the dye ions are well and truly charged, having four unit charges upon each. All neutral electrolyte has been removed. Now when many insoluble solids are put into water they acquire quite a strong negative charge, relative to the water, on the outer wetted surface. The range and the strength of attractions or repulsions set up by this charge are similar to those of the charges on dye ions, sodium ions, etc. All textile fibres acquire this surface negative charge in distilled water. Thus when a negatively charged dye ion comes near the surface of negatively charged cellulose, there is electrostatic repulsion, always set up between bodies bearing charges of the same kind, and the dye ion is pushed away from the surface of the fibre. How effective this push may be depends upon the conditions ruling at the time, especially upon the speed with which the dye ion is moving. If it is moving slowly, then it will be pushed right away from the surface and will, on that occasion, have no chance of being adsorbed. This charge on the surface does provide a real obstacle or barrier to the free entry of dye ions; hence the name that has been given to it. Should the ion be moving fast, then, although the repulsion which it experiences as it nears the charged fibre surface will slow it down, it will not be stopped completely, and has a chance to get to the fibre and so to be adsorbed. The first ion has been stopped by the fence; the second has rushed it. When we talk of a "potential barrier", our attention is drawn specifically to electrical potential, but the general principles of potential difference which were discussed in Part I[1] apply quite as strictly here. If an anion with a single unit of charge upon it is brought up from the outer solution to the surface of the cellulose, there will be a repulsion, as we have seen, and if we are determined to take the ion to its destination we shall have to do work. The greater the intensity of charge upon the cellulose the more work we shall have to do, and the greater the potential difference between the fibre and the solution. In the actual process, the greater this potential difference the faster will the ion need to approach, i.e. the greater must be its energy of movement, to overcome the repulsion completely. In thinking about these things, there is a tacit and quite sound tendency to regard this electrical charge on the fibre as if it were a material barrier, the height of which is defined by the potential difference existing at the interface with the dyebath. When ions possess the necessary energy of movement to enable them to get over the barrier they are said to be *activated*.

One implication of this theory will be seen at once. Among all the dye ions that are present in a dyebath, only a fraction, the fast moving, activated ones, are available for dyeing, so that the effective concentration is much less than the actual concentration. Another is that, for a barrier of a given "height"— a potential difference of a given value at the surface— the ions of some dyes will be repelled more and will have more difficulty in getting through than the ions of others. For instance, Sky Blue FF, with its four charges on the ion, will require more activation to rush the barrier than will Chrysophenine G, which has only two. It is not difficult to understand, therefore, why the former, when dyed without any addition, should have a low exhaustion, independently of concentration effects with the accompanying sodium ions (Donnan effect).

It is possible to estimate, from knowledge of the fundamental properties of solutions, how many among the total number of dye ions in a solution will, under specified conditions, be available for dyeing, i.e. will possess the requisite energy of motion. The situation within a solution of electrolyte is roughly as follows. The water molecules and all the ions are moving about very rapidly, at an average speed which depends on the temperature. There is no special direction in their movement if the solution is kept still, their individual movements being quite at random. The energy of each particle depends on its speed and its weight. When any two come close enough there is a collision, and they shoot off in different directions at different speeds, so that the former total energy of the two is redistributed among them. One may get the worst of the encounter and may go off at great speed; then the other one will have to lumber away more slowly. With millions of these encounters taking place every second, it will be seen that there will be present in the solution particles moving at all rates from very slow to very fast, with corresponding ranges in the energy content. Although, for selected particles, the picture changes from instant to instant, there are so many particles and the encounters are so frequent that the distribution of speeds and energies, for all the particles taken together, remains constant. Statistical rules apply here with greater validity than they do, for instance, in the incidence of births and deaths in a large population, the accurate calculation of which enables insurance companies to make a living and even to pay dividends. Providing that there is nothing, no outside interference, to prevent the molecular and ionic movements from happening completely by chance, the fraction of molecules having an energy

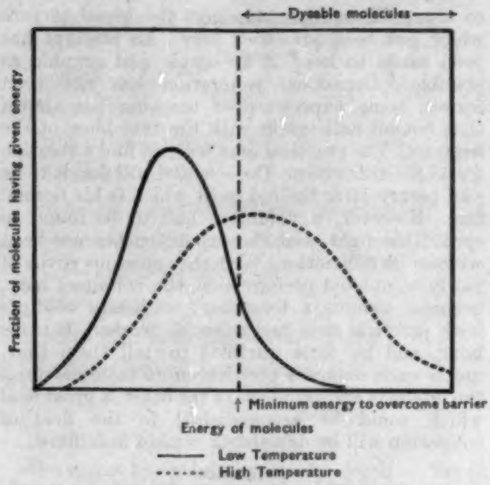


FIG. 3

content greater than a specified value can be calculated. The type of distribution is shown in Fig. 3, in which the size of the fraction having a particular energy is plotted against this energy content. If the temperature increases, and all the particles are speeded up, a fresh curve will be formed corresponding to an increase in the total energy, but the characteristic shape will be little changed.

Thus, in a specified dyeing experiment, if the surface potential difference is known, together with the number of charges on the ion, the amount of energy a dye ion must possess in order to get over the barrier, and thus to be available for adsorption by the fibre, can be calculated. Then from the energy distribution calculations it is possible to find out how many of the dye ions will be activated and will qualify for dyeing. Experimental measurements of the surface potential difference are not easy to carry out directly, especially at the temperatures customary for direct dyeing. A great deal of very careful and patient work on the subject has been done by Neale and his collaborators. It has been found that, in the dyeing of cellulosic fibres with a bivalent dye like Chrysophenine G at room temperatures, perhaps only one in every hundred dye ions in the solution will be sufficiently activated to get over the barrier. Hence it could be said that this dyebath is only about 1% efficient for dyeing purposes.

GETTING OVER THE POTENTIAL BARRIER

If the problems of overcoming the restrictive effects of the barrier are viewed in terms of the hunting field, it will be seen that the possible approaches resemble those taken by riders of different experience and temperament. When the fence is high, the dashing rider with the good horse will take a long run, whip his horse up ("activation" is not a bad term), and get all the speed and height he can to enable him to clear the obstacle fairly. The canny man will look for a gap in the fence, or even, at the risk of ostracism, try pulling it down. These alternatives exist in some measure in dyeing. Raising the temperature will raise the total energy of all the dye ions, so that the proportion which can get over the barrier will be made greater. Within the ordinary range of dyeing temperatures, this effect alone, though it will help, cannot give a very great proportional advantage. One of the reasons for this is that the temperature has to be calculated from absolute zero, −273°c., the condition of a body with no heat in it at all. If the temperature of a dyebath is raised from 50°c. to 100°c., we may feel that we have doubled the temperature and that effects depending on temperature may double in magnitude also. If, however, we can only say that we have gone from 323° above absolute zero to 373° above it, the expected increase is not nearly so great. This factor will be more significant if some of the methods for dyeing under pressure, at temperatures well above 100°c., become common.

Fortunately it is easy to pull down the fence. As a matter of direct experimental observation, it is found that, if a neutral electrolyte is added in moderate proportions, a few per cent of sodium chloride, the potential difference between the fibre and the bath is made very small, so that the energy content necessary in a dye ion for it to get through the lowered barrier is greatly reduced. It is not too easy to explain in terms of mechanical analogies why this should be so, and in the attempt one of our former analogies may need to be modified. We have spoken about pulling down the fence. This is not accurate, for whatever the moderating effect of the presence of an electrolyte like sodium chloride, the mechanism by which the potential barrier was first formed is unlikely to have gone out of action; it has only been overwhelmed. Perhaps the situation can be put in this way. When sodium chloride is added to the solution, the ion population is much increased; positive sodium ions and negative chloride ions, small in size, rapid in movement, not capable of attachment to the fibre by hydrogen bonds, come to take part in the general interplay of electrostatic attractions. They can readily get on either side of the fibre surface, and the chloride ions can suffer some of the repulsive effect formerly suffered by the dye ions alone. The sodium ions can be attracted to the negatively charged surface in greater numbers and can neutralise some of the repulsive surface effect until the dye ions get very near. Thus the constituent ions of the salt can be likened to clods of earth which might be piled up in sloping banks at either side of the fence, so that the horse can be walked over instead of having to take a heroic leap.

As was said at the beginning of this story, we are still very much in the position of confirming by theory what the dyer already knows by practice, rather than of predicting by theory new events unknown in industrial technology. The last two theoretical developments have illustrated this very well, substantiating in detail the beneficial effects of sodium chloride and similar salts in direct dyeing. It is, in fact, very fortunate that this valuable assistant is to hand, for some will perhaps have seen that the restriction of dyeing by the surface potential difference is

an effect which the dyeing process itself will aggravate. With some dyes, which have a relatively low valency and high chemical affinity for the fibre, some dyeing does take place in the absence of salts. When a dye ion is first attached to the cellulose through its hydrogen bonds, at the periphery of the fibre, its negative charges add to the charge produced when the fibre was first put into water. Thus the barrier increases in obstructive effect as dyeing goes on, and it is unlikely, therefore, that the direct dyes, when they were first discovered, would have had any value but for the action of salt, whether accidentally or deliberately introduced.

* * *

There are many other things of intense theoretical and practical interest in the present-day growth of a consistent groundwork of ideas about dyeing, linking familiar traditional operations with phenomena observed and investigated in other fields through the generalised principles of science. It is hoped that other specialists may, from time to time, fill more details into the broad picture which has been presented here. An attempt has been made to keep it as simple and graphic as possible. Occasional reiteration has not been feared: some experience of teaching has shown that not all nails go in with the first blow of the hammer. The practical man will not find a solution for all his difficulties. The scientist will find it to be puff pastry after the red meat which is his normal fare. However, a volunteer had to be found to spread the light, and the exposition has not been without its difficulties. With the conscious virtue of newly completed performance, the volunteer may, perhaps, assume a temporary authority towards both practical man and scientific worker. It is his hour, and he feels qualified to tell them that, unless each makes a positive effort to understand the interests and problems of the other, a great deal which could be accomplished in the field of coloration will be delayed or remain unfulfilled.

Reference

[1] Turner, J.S.D.C., 71, 29 (Jan. 1955).

ERRATUM. Theories of Dyeing—I, by H. A. TURNER (J.S.D.C., 71, 37 (Jan. 1955))— In the formula at the foot of the second column, "H^+" should be B^+.

Notes

Election of Fellows and Associates

At the Meeting of Council held on 12th January 1955, the following were elected either Fellows or Associates of the Society.

FELLOWS

Brojendra Chandra Bhattacharya
(Serampne, West Bengal, India; Principal of the Bengal Textile Institute)

Simon Borton
(St. Kilda, Victoria, Australia; Consulting Chemist, Research Laboratory for the Fur Industry)

Samuel Burgess
(Glossop, Derbyshire; Technical Manager, Messrs. Courtaulds Ltd., Droylsden)

Malcolm Victor Campbell
(Kidderminster; Head Dyer and Chemist, Messrs. T. Bond Worth & Sons Ltd.)

Chauncey Eugene Coke
(Montreal, Canada; Manager, Industrial Yarn Sales and Development, Messrs. Courtaulds (Canada) Ltd.)

Archibald John Hall
(Somerton, Somerset; Consulting Dyer and Finisher)

Arthur Jacob Immins Harding
(Leicester; Chairman, Messrs. Fosse Dyeworks & Maifosse Ltd.)

William Johnson
(Leicester; Chairman and Managing Director, Messrs. Hawley & Johnson Ltd.)

Ernst Kornreich
(London; Technical Manager, Messrs. Trubenised (Great Britain) Ltd.)

Robert James Sheddon Linn
(Wolverhampton; Manager, Dyeing and Finishing Works, Messrs. Courtaulds Ltd., Wolverhampton)

Robert Arthur Peel
(Helensburgh, Scotland; Dyehouse Manager, The United Turkey Red Co. Ltd.)

George Rowntree Ramage
(Huddersfield; Head of Department of Chemistry, Colour Chemistry, and Dyeing, Huddersfield Technical College)

Reginald John Roberts
(Leicester; Director, Messrs. Hawley & Johnson Ltd.)

ASSOCIATES

Norman Baxter
(Carlisle; Assistant Print Works Manager, Messrs. Ferguson Brothers Ltd.)

John Rufford Clegg
(Halifax; Apprentice Dyer, The Bradford Dyers' Association Ltd.)

Arnold Malcolm Jowett
(Sowerby Bridge, Yorkshire; Apprentice Dyer, The Bradford Dyers' Association Ltd.)

Denis Michael Nunn
(Works Chemist, The Bradford Dyers' Association Ltd.)

Geoffrey Pullan Pearson
(Guiseley, Yorkshire; Garment Dyers Works Chemist, Messrs. Jas. Smith & Sons Ltd., Ravensthorpe, Yorkshire)

Meetings of Council and Committees

January

Council— 12th

Finance— 4th

Publications— 18th

Diplomas— 12th

Diplomas Executive Subcommittee— 26th

Colour Index Editorial Panel— 4th and 13th

Terms and Definitions— 6th

Perkin Centenary— 7th

Perkin Centenary Executive— 21st

Northern Ireland Symposium— 15th

Deaths

We regret to record the loss by death of Mr. S. Bannister, Mr. W. M. Campbell, Mr. J. C. Gray, and Mr. L. W. Pickup.

Honorary Secretary of the Terms and Definitions Committee

The Committee has accepted with great regret the resignation, tendered on health grounds, of Mr. H. C. Olpin as its Honorary Secretary, and has recorded its deep appreciation of his services. Mr. S. R. Cockett has kindly consented to fill the vacant office.

The British Association

Professor Sir Robert Robinson, O.M., F.R.S., M.A., D.SC., LL.D., has been elected President of the British Association.

Expansion of the British Dyestuffs Industry

Mr. Harry Jackson, Joint Managing Director of I.C.I. Ltd., Dyestuffs Division, in an interesting article in the *Financial Times* of 22nd November 1954, has given the following figures (in £1000) of the value of the dyes exported by all the major exporting countries (Germany, Switzerland, United Kingdom, France, Italy, U.S.A., and Japan) and by the U.K. alone—

Year	Total	U.K.
1937	20320	1495
1947	42619	7712
1950	59487	10183
1951	76028	10565
1952	44307	8085
1953	57062	9115
1954*	34039	5572

1937 was the peak pre-war year. Whilst the total had increased to 335% of the pre-war level, exports from the U.K. alone had increased to 745%.

H. E. N.

* Jan.-June only.

Cellulose Triacetate Textiles

Several firms have recently announced the production of yarns and staple fibres of cellulose triacetate. The new fibre can be permanently set by heat-treatment processes, so that it is especially suitable for garments that can be washed easily and require little ironing. Cellulose triacetate has a high melting point (about 300°C.), low water imbibition, and high resistance to chemicals and weathering. It can be dyed with disperse dyes, but these are absorbed more slowly than by acetate rayon. It can be blended with other fibres.

Among trade names under which cellulose acetate is marketed are Courpleta (Courtaulds), Tricel (BrC), Arnel (Celanese Corpn. of America), and Trilan (Canadian Celanese).

New Books and Publications

Die Praxis der Färberei

Erfahrungen Rezepturen und Winke

By F. Weber and F. Gasser. Pp. xii + 851, with 347 illustrations in the text. Vienna: Springer-Verlag. 1954. Price, 187s. 6d.

No short review can do full justice to this monumental work, either in its many solid merits or in its occasional defects. There are, indeed, few critics with a personal experience sufficiently far-ranging to enable them to deal adequately with all parts of the book. The treatment is certainly encyclopaedic, but, unlike many of the major works on textile processing subjects that have come recently from the Continent, the authors have set out primarily to deal with the actual practice of dyeing operations, and to give the dyer some lead in almost all his interests and some help in most of his difficulties. Much of the work is based on personal experience. These parts of the book are generally easy to identify and are the most acceptable. However, it is obvious that no pair of authors could invoke personal experience for every topic in so comprehensive a scheme. Dr. Weber and Dr. Gasser have therefore ranged very widely through the technical literature of the world, have, on the whole, selected the spoils fairly, and have arranged them effectively. Incidentally, since the selection has been reasonably objective, this book reflects, unconsciously one would imagine, the great preponderance of American contributions to technical dyeing literature in English when the emphasis is laid on practical working directions rather than on general or theoretical aspects.

Some of the less common treatments stem from the practical outlook with which the book was planned. There is, for instance, a long section which treats of the planning, organisation, and economics of commission dyeworks as well as

dyeing departments in vertical textile concerns. Many examples of recording and costing procedures are included, for various classes of goods. These serve as patterns and also give some interesting insights into the dyeing operations themselves, but the actual figures are of historic interest only, for most of them come from Austrian and Czechoslovakian sources and refer to periods before the last war. In this "management" section is an article, commonsense rather than inspired, on accident prevention, and one on the equipment and running of a laboratory. On the latter topic, the authors have rather let the subject run away with them, and have detailed minutely the equipment of a fairly well stocked laboratory on a pattern which most chemists, textile or otherwise, would choose instinctively. The main value of the catalogue might be as an authoritative backing for the chemist wanting to get some reasonable range of tools from a frugally minded executive. In equipment for control-dyeing and dye-testing the selection tends to be old-fashioned. Some of the modern, and very useful, modifications of normal dyepot equipment, incorporating thermostatic control and mechanical agitation, do not seem to have been heard of. There is scarcely any reference to photoelectric colorimeters and absorptiometers, although these would surely be chosen now in preference to visual instruments. There does not seem to be a mangle of any kind.

On the industrial scale, descriptions of dyeing plant and procedures are often very good, and may contain unusual information about methods which is of great value and interest. These descriptions are illustrated well with small but clear sketches. There is a certain disproportion in the attention given to the different branches of dyeing. The treatment for yarn dyeing is much fuller and more detailed, and reflects a greater amount of direct experience than does that for piece dyeing. The jigger, particularly the modern "tensionless" version, surely merits more discussion than it receives here. The importance of continuous systems for piece dyeing with vat dyes is recognised, but the discussion is not very full or critical. This does not apply to the Standfast machine, which is treated with greater scepticism than it really deserves, probably because one or two of the principles of its operation do not seem to be fully appreciated.

There is a similar disproportion between the treatments of protein and cellulosic fibres, the latter, in view of the volume of goods processed and the special difficulties of dyeing, not receiving quite so full attention as they should. Among the protein fibres, there is a section on silk preparation and dyeing that is fuller and more detailed than is usual for general dyeing books.

With very laudable feeling for dyers of the future, the authors have made strenuous efforts to include all possible information about the dyeing of fully synthetic fibres, and this should prove helpful in all branches of the trade. Their enterprise is also shown by the inclusion of a fairly full section on the dyeing of fibre mixtures; and the garment, knitwear, and hat industries are not left out.

A section on faults is bound to be discursive if it is founded on personal experience, and it would be overexacting to demand that it should be strictly systematic. Many of the examples discussed should provide a clue for the investigation of out-of-the-way faults which have not yielded to routine methods of attack.

A distinctive feature is the frequent photographic reproduction of pattern cards to illustrate fabric or yarn styles, the results of tests, or defects. The experiment is an interesting one, and much care seems to have been taken in the photomechanical reproduction of the specimens, but it cannot be said that monochrome half-tone is always able to cope with subtle distinctions in appearance that the authors may sometimes wish to bring out. A more consistently successful feature is the copious tabular display of information. Very complete lists are given of the chemical composition, provenance, and simple properties of every fibre, natural and manufactured, of any significance to the dyer. There is also a large and very sensible select list of dyes, in every application class, and for every type of work, with the names of equivalent commercial products for all the important European and American manufacturers. Beyond its value for direct reference, this list is interesting in showing clearly what each maker is contributing to the full palette of the dyer. There are short vocabularies of German, English, and French technical terms. The English one needs a fair amount of correction in any future edition.

It is rather a pity that the high cost of this book, for which the exchange rate and not the publisher must be blamed, and the language in which it is written, will keep it from many practical men in this country, who would find it both useful and very interesting. It has no real counterpart in modern dyeing literature.

H. A. Turner

Heterocyclic Compounds with Indole and Carbazole Systems

By W. C. Sumpter and F. M. Miller. Pp. xii + 307. New York and London: Interscience Publishers. 1954. Price, $10.00.

Dealing as it does with structures on which some of the very basic principles of organic chemistry have been built, i.e. with classical organic structure theory, and with a wide and varied range of compounds, this eighth volume is probably the one of most general interest, so far to have appeared in this series of monographs, on The Chemistry of Heterocyclic Compounds. The first chapter deals with indole and the many fascinating problems it has presented as its chemistry has developed, since Baeyer's pioneer work in the 1860s. The treatment is factual and precise, and throughout the whole book extensive literature references are given. As far as can be judged, these are adequate and usually complete; in fact, documentation frequently occupies as much space on the printed page as the descriptive matter to which it refers.

Chapter II is one of the best concise accounts of the chemistry of carbazole in existence. The only authoritative book on this topic is that of Cohn published in 1919 and, although review articles have appeared from time to time since that date, a concise up-to-date account of this topic was definitely needed. It is clear from these two chapters what an important contribution the British schools of chemistry, and in particular that of Oxford, have made to indole and carbazole chemistry.

Again, in Chapter III it is useful to have a complete up-to-date account of the work on isatin; admittedly a great deal of it was done in the latter half of the last century, but this early work has been greatly extended and clarified in the last thirty years. Short, but no less interesting, chapters (IV and V) follow on oxindole and isatogens, those nitrones whose exact structure has only recently been adequately explained.

It may surprise readers of this *Journal* that the important compounds indoxyl and indigo are dealt with in about thirty pages (Chapters VI and VII), but all the essential chemical points are clearly and well expressed, even the fact that the colour of indigo is still a problem; the only omission possibly worthy of comment is that of the sulphate ester of leuco indigo, the discovery of which was an important contribution to dye chemistry. The last chapter, comprising about a third of the whole book, deals with the ever increasing list of over fifty natural products containing the indole nucleus, viz. the indole alkaloids, ranging from the relatively simple gramine, 3-(dimethylaminomethyl)indole, and tryptophan to extremely complex molecules like yohimbine and strychnine. Thus the interest of indole derivatives extends from dyes, through the most potent drugs, to the chemistry of living cells. To have treated the chemistry of all these compounds so extensively and so lucidly in a book of such reasonable dimensions is a most creditable performance, on which the two authors and their editor are to be congratulated. As usual the book is clearly printed and well produced, although there are a few minor printing errors, but of such an obvious character as not seriously to interfere with the accuracy of the text. S. COFFEY

Selenium

A Short Review of its Production and Utilisation with reference to the Current Shortage

By R. Ashton, E. G. Hill. and D. Neville-Jones. Pp. 29. London: H.M.S.O. 1954. Price, 1s. 6d.

Because of increased demand from the glass and electrical industries there is now an acute shortage of selenium; for this reason the D.S.I.R. undertook this technical review of the production and utilisation of selenium and its compounds. The two sections that will interest readers of the *Journal* most are those on the use of selenium in the glass industry, both as a decoloriser for ordinary white glass and as the colouring agent in ruby glasses, and on its use as a pigment, principally in the form of cadmium sulphoselenide. The employment of these pigments in plastics— the largest single use is in polyvinyl chloride, for which there seems to be no practical alternative to cadmium sulphoselenide as a red pigment— paints, rubber, vitreous enamels, printing inks, and artists' colours is surveyed.

Reference (9) to Curtis and Wright's paper on cadmium pigments is wrongly quoted; it should be *J. Oil Col. Chem. Assocn.*, **37**, 26 (1954).

C. O. CLARK

Abstracts from British and Foreign Journals and Patents

The titles of abstracts may be modified. Abbreviations of names of firms are listed in J.S.D.C., **68,** *23 (Jan. 1952), and also, together with symbols and the periodicals abstracted, in the annual index*

I—PLANT; MACHINERY; BUILDINGS

Barotor Loading Improvement. P. M. Cole. *Amer. Dyestuff Rep.*, 43, 709–711, 735 (25 Oct. 1954).

The initial Barotor pressurised piece-dyeing machines necessitated special handling to form batches of nearly equal lengths. A device is now described in which, by means of a scray and plaiter, the fabric is folded automatically into a suitable number of layers, making a folded length equal to the length of the fabric path of one wrap on the Barotor. Loading and unloading are thus greatly simplified. The Barotor itself is simplified by elimination of a large proportion of the fabric-supporting bars, as adequate penetration through many unsupported layers of material has been found to result from the paddle-like rotor action. Bar movement has also been eliminated, the angle at which the fabric enters and leaves the liquid being adjusted so that the weight of liquid picked up during rotation is sufficient to advance the fabric quite effectively. J. W. B.

PATENTS

Applying Liquids to Slivers, etc. Bachmann Uxbridge Worsted Co. *USP* 2,660,763

A means for applying wool creams or sighting colours. C. O. C.

Yarn Sizing and/or Dyeing. S. Rivetti. *BP* 718,460

Apparatus in which the yarn is unwound from bobbins, sized and/or dyed, dried and wound on cross-wound conical bobbins. C. O. C.

Physical and/or Chemical Treatment of Warps or Fabrics. Gebrueder Sucker. *BP* 718,415

When treating with hot gas or vapour the processing speed can be much increased and less heat wasted if the material while passing through the processing zone is treated with a stream of the gaseous agent in either the same or in counter current direction. The speed of flow of the gas is speeded up so that treatment takes place with such physical values that the Reynolds number is greater than the critical Reynolds number. C. O. C.

Drying with Superheated Steam. J. Dungler. *BP* 718,418

The material is treated in separate zones with superheated steam, the steam in each zone being continuously withdrawn, reheated and fed back to the treating zone, a portion of it being fed to a condensation chamber branching off the main steam circuit. C. O. C.

Feeding Excess of Fabric into Stenter Clips. J. Dungler. *BP* 718,434

A device for introducing the fabric into the clips with an advance lead so as to compensate for shrinkage occurring while the fabric is held in the clips. C. O. C.

Nozzle and Roller Arrangements for Tensionless Driers. J. Dungler. *BP* 718,841

Machine for Producing Multi-coloured Prints Simultaneously on Both Sides of a Fabric. M. Stead. *BP* 719,897

Screen Printing Machine. R. R. Laupman. *BP* 718,459

A machine in which all the operations are carried out automatically by mechanical means, i.e. without any electrically actuated parts. C. O. C.

Screen Printing Machine. Luminous Processes. *USP* 2,662,470

A fully automatic machine which prints several articles or pieces of work at once. C. O. C.

Coating Sheet Material. A. L. Gibbs. *BP* 718,513

Excess molten coating composition is projected on to the under surface of a web of paper from a nozzle comprising a horizontal duct having a narrow slot or a series of closely-spaced holes so that the coating is continuous when it reaches the web. The temperature of the liquid is only slightly above its solidifying temperature, and excess coating is scraped off before it solidifies by a scraper set close to the point of application and returned to circulation. The uncoated side comes in contact with a chilling roll immediately afterwards to solidify the coating rapidly. The process may be used to apply a protective film to a hectographic carbon paper already coated with the hectographic transfer coating. S. V. S.

Extracting the Liquid from Fabrics in Drum Washing Machines. Avco Manufacturing Corpn. *BP* 718,863

Adherence of the materials to the surface of the drum is prevented by removing the major portion of the rinsing liquid at a speed between those used for washing and extraction respectively, allowing the materials to break away from the drum by slowing or stopping rotation and then extracting the remaining excess liquid at high speed. C. O. C.

Drying Stockings in Stacks. Smith, Drum & Co. *USP* 2,664,647

Garment Press. W. Goldman. *USP* 2,663,954

An automatic steam press particularly suitable for treating knitwear operates in a predetermined cycle under the control of a master motor and push button. C. O. C.

Electrostatic Coating Method and Apparatus. Ransburg Electro-Coating Corpn. *USP* 2,662,833

A simple machine for electrostatically coating the exterior of hollow objects without use of backing electrodes especially shaped for the objects to be coated. C. O. C.

III—CHEMICALS; AUXILIARY PRODUCTS; FINISHING MATERIALS

Thiourea Dioxide (Formamidinesulphinic Acid) as an Organic Reducing Agent. P. H. Gore. *Chem. and Ind.*, 1355 (30 Oct. 1954).

Thiourea dioxide reduces aromatic nitro, azoxy, azo, and hydrazo compounds to the amines, quinones to quinols, and many dyes to their leuco derivatives; good yields are obtained. Ketones and α-diketones are unaffected. Reductions may be carried out using water, pyridine, dimethylformamide, or mixtures of these in the presence of excess ammonia or caustic alkali. The reagent is oxidised to the formamidinesulphonic acid stage. J. W. D.

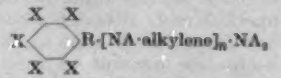
PATENTS

Stabilising Hypochlorite Solutions. Standard Oil Development Co. *USP* 2,662,858

Addition of 0·01–0·10% of $K_2Cr_2O_7$ to solutions of alkali metal hypochlorites stabilises them even in presence of heavy metals, e.g. iron. C. O. C.

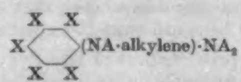
Metal-sequestering Agents. F. C. Bersworth. *BP* 718,848

Compounds of formula—



(X = H, Alk, alkoxyl, OH or Hal, at least 3X being Hal; R = divalent alkylene of 1–5C and may contain an interrupting ether O atom; alkylene = $CH_2{\cdot}CH_2$, $CH_2CH_2CH_2$ or $CH(CH_3)CH_2$; n = 1–5; A = CH_2COOM or CH_2CH_2COOM (M = H, alkali metal, NH_4 or subst. NH_4) are effective sequestering and germicidal agents over a wide range of pH particularly as the number of COOH groups in the alkylene polyamine increases. When no R group is present and n = 1, the phenyl group prevents strong chelation particularly with alkaline earth ions. When R = CH_2 the tendency for chelation is very high; as the chain length of R increases the stability of the chelates decreases somewhat but still remains high. *BP* 719,901

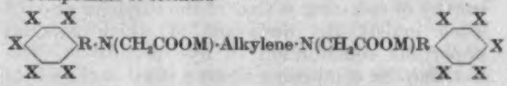
Compounds of formula—



have similar properties. C. O. C.

Substituted Aralkyl Alkylene Diamino Diacetic Acids and their Salts—Sequestering Agents. F. C. Bersworth. *BP* 718,849

Compounds of formula—



(R = alkylene of 1–5C and may contain an interrupting ether O atom; Alkylene = $CH_2{\cdot}CH_2$, $CH_2{\cdot}CH_2{\cdot}CH_2$ or $CH(CH_3){\cdot}CH_2$; X = H, OH, Alk, alkoxyl or Hal, 1–3 of the X groups of each phenyl nucleus being Hal; M = H, alkali metal, NH_4 or subst. NH_4) are soluble in both water and organic solvents. In both solutions they have strong chelating properties towards heavy metal ions and have bactericidal and fungicidal properties. C. O. C.

Flame-resisting Agents. Glenn L. Martin Co. *USP* 2,660,542–3

Flame-resisting finishes fast to laundering and dry cleaning and which do not affect the handle of the treated material are produced by applying an organic flame-resisting agent which upon polymerisation provides its own resinous binder, e.g. triallyl phosphate polymerised and then brominated. Preferably polymerisation and/or if necessary halogenation, is carried out directly on the material to be rendered flame-resisting. C. O. C.

Chromium Co-ordination Complexes of Saturated Perfluoromonocarboxylic Acids—Water- and Oil-repelling Agents. Minnesota Mining & Manufacturing Co. *USP* 2,662,835

The chromium co-ordination complexes of sat. compounds of formula $C_nF_{2n\pm1}COOH$ (n = 3–9; the COOH group can be linked either to a cyclic or a non-cyclic C atom), e.g. perfluoro*cyclo*hexane acetic acid or *n*-heptafluorobutyric acid, are green solids, slightly soluble in water and highly soluble in acetone and alcohols. They yield extremely thin, firmly adhesive, water- and oil-repellent greenish films on a variety of surfaces, e.g. textiles, paper, glass, metals, etc. C. O. C.

Size or Finish for Textiles, Paper, Regenerated Cellulose Sheeting, etc. C. Schlatter, J. B. Eisen, and G. D. Jefferson. *USP* 2,663,989

A waxy partial ester of an anhydropolyhydric alcohol, e.g. sorbitan mono- or dipalmitate, is dispersed in water in presence of a water-soluble or dispersible binding colloid, a polyoxyethylene ether of castor oil or hydrogenated castor oil containing 80–200 ethoxy groups in the molecule and an alkaline buffer. The product is used for sizing and lubricating yarns or for treating tyre cords before applying rubber latex. C. O. C.

Solvents for Polyacrylonitrile. Courtaulds. *BP* 718,997

A mixture of a solution of LiBr, LiI; NaI or $ZnCl_2$ in acetonitrile and/or acetone with water and/or an aliphatic monohydric alcohol of < 7C and/or ethyl lactate is a good solvent for polyacrylonitrile. Preferably there should be at least 35% by wt. of salts in the mixture. C. O. C.

Aqueous Halogenoacetonitriles as Solvents for Polyacrylonitrile. Chemstrand Corpn. *USP* 2,660,571

Although neither halogenoacetonitriles nor water dissolves polyacrylonitrile a mixture of the two is a very effective solvent, e.g. a mixture of 70–99% chloroacetonitrile and 30–1% of water. C. O. C.

Solvents for Acrylonitrile Polymers. BrC. *BP* 720,199

Copolymers of 85–94% by wt. of acrylonitrile and 15–6% of lower alkylacrylic acid or lower alkyl esters of acrylic acid readily dissolve in nitromethane containing ≯3% of water. C. O. C.

Synthetic Tanning Agents. Monsanto. *USP* 2,663,698

Tanning agents which yield a white leather are obtained by dehydrating a novolak resin, and then sulphonating until a water-soluble product is obtained, both treatments being carried out under sub-atmospheric pressure. C. O. C.

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p-Nitrophenol as a Fungicide for Leather (XII p. 120).

IV—RAW MATERIALS; INTERMEDIATES; COLOURING MATTERS

Simplified Wolff-Kishner Reduction. G. Lock. *Mh. Chem.*, **85**, 802–806 (Aug. 1954).

The improved method, applied only to carbonyl cpd. more readily reducible because they contain hydroxyl groups, consists in refluxing them for a short time with hydrazine hydrate, cooling, adding powdered KOH, and reheating until nitrogen is no longer evolved. Yields are 80–90%. H. E. N.

Behaviour of Nitrobenzene with Percarbonic, Perboric, and Perchromic Acids. R. B. Heslop. *Chem. and Ind.*, 1487 (27 Nov. 1954).

Unlike pernitrous acid, neither percarbonic nor perboric acid shows signs of hydroxylating nitrobenzene, but perchromic acid does hydroxylate, though the reaction is only just detectable. H. H. H.

Steric Effects on Mesomerism. XIII—Preparation of 2:6-Dimethyl-4-nitroaniline. B. M. Wepster. *Rec. Trav. chim.*, **73**, 809–818 (Sept.–Oct. 1954).

Nitration of 2:6-dimethyl-*p*-toluenesulphonanilide or 2:6-dimethyl-benzenesulphonanilide in aq. acetic acid, followed by deacylation, gives 2:6-dimethyl-4-nitroaniline in yields of 80–90%. A cold mixture of HNO_3 and acetic anhydride brings about, after prolonged standing (one year), the nitration of 2:6-dimethylacetanilide (I) in the 4-position, but only to the extent of a 10% yield. Stronger nitrating agents, if used to improve the yield, give rise to an ultimate preference for the 3-position. This, and other evidence (which is discussed), confirms that in I there is steric inhibition of the aniline mesomerism, with consequent low reactivity in the 4-position. Although the formyl group is smaller than the acetyl, 2:6-dimethylformanilide undergoes nitration predominantly in the 3-position. With 2:6-dimethylbenzylideneaniline, in which the electron structure and valency deflections are favourable to substitution in the 4-position, nitration does indeed occur in that position, though the yield is only 15%. Under strongly acidic conditions, nitration in the 3-position occurs. Nitration of 2:6-dimethyl-*p*-toluenesulphonanilide proceeds smoothly, and with good yield, in the 4-position; the mechanism is discussed. The deacylation rate constant of 2:6-dimethyl-4-nitroacetanilide in a boiling methanol soln. of Na methoxide affords evidence of a very considerable steric inhibition of the mesomerism. The experimental work is given in full detail. J. W. D.

Absorption Spectra and Molecular Structure. II—Alcoholic Solutions of Chloroanilines. A. A. Kharkharov. *Izvestiya Akad. Nauk S.S.S.R., Otdel. khim. nauk*, 854–858 (Sept.–Oct. 1954).

Absorption spectra are detailed, graphically and in tables, for alcoholic soln. of 11 mono-, di-, tri-, and tetrachloroanilines over the range 210–350 mμ. The bathochromic effects of the chloro substituents are very nearly additive. A. E. S.

Preparation and Constitution of some Benzene Derivatives containing the Acetylamino and Methylsulphonyl Groups as Substituents. J. Bolssens, J. A. C. T. Brouwers, J. H. Choufoer, A. Kats, P. E. Verkade, and B. M. Wepster. *Rec. Trav. chim.*, **73**, 819–841 (Sept.–Oct. 1954).

Syntheses and proofs of constitution of numerous cpd. are given, together with full practical details. J. W. D.

Dissociation Constants of o-Aminophenol. E. Schauenstein and G. M. Perko. *Mh. Chem.*, **85**, 580–587 (June 1954).

A basic dissociation constant of $5{\cdot}0 \times 10^{-10}$ and an acid one of $1{\cdot}1 \times 10^{-10}$ were determined spectrographically. H. E. N.

The Coupling Reaction. VIII—The Form of Diazo Compounds at Various pH Values. Coupling in strongly Alkaline Medium. C. Wittwer and H. Zollinger. *Helv. Chim. Acta*, **37**, 1954–1968 (Dec. 1954).

From kinetic studies of the coupling of diazotised metanilic acid or *p*-chloroaniline to NW, Schäffer's β, or G acid at various pH values, it is shown that the diazonium ion acts as a dibasic acid, the first dissociation constant of which is very much smaller than the second. It follows that, when the point of rearrangement is reached, the diazonium ion is converted directly into the normal diazoate, the intermediate diazo hydroxide being formed in vanishingly small amount. In the pH region 4·5–13·2, the coupling velocity is proportional to the diazonium ion concn., which decreases to about 1% for every pH unit above the point of rearrangement. The diazoate couples either not at all or only very slowly, and as the diazo hydroxide is present in aq. soln. in only extremely small proportion, its coupling power cannot be investigated. H. E. N.

Radioactive Butter Yellow. W. Zischka, K. Karrer, O. Hromatka, and E. Broda. *Mh. Chem.*, **85**, 856–863 (Aug. 1954).

Butter Yellow, *p*-dimethylaminoazobenzene, labelled with radioactive carbon in the *o'*-position, was fed to rats, and the distribution of the radioactivity in the body was followed. H. E. N.

Induction of Tumours with 1-(2-Tolylazo)-2-naphthol (Oil Orange TX). G. M. Bonser, D. B. Clayson, and J. W. Jull. *Nature*, **174**, 879–880 (6 Nov. 1954).

Tumours are induced in mice by injecting them with a solution of Oil Orange TX in arachis oil, and it is suggested that because of its carcinogenic activity the use of this dye as a food colorant should be discontinued. J. W. B.

Azo Dyes and their Intermediates. XII—Syntheses of Dyes in the Benzo Fast Yellow RL Series. T. Nishi, Y. Abe, and K. Takagi. *J. Chem. Soc. Japan, Ind. Chem. Sectn.*, **56**, 367–369 (1953): *Chem. Abs.*, **48**, 10347 (10 Sept. 1954).

4-Aminoazobenzene-4'-sulphonic acid and its 3-methyl, 2-methyl, 3-methoxy, and 5-methoxy derivatives were treated with $COCl_2$, and the properties of the resulting yellow direct cotton dyes examined. Those dyes with an *o*-methyl or *o*-methoxy group were particularly valuable. E. S.

Azo Dyes from Catechol. V. I. Kuznetsov and A. A. Nemodruk. *Sbornik Statei Obshchei Khim.*, **2**, 1378–1381 (1953): *Chem. Abs.*, **48**, 10347 (10 Sept. 1954).

Catechol was successfully converted into its azo derivatives by carrying out the coupling with diazo compounds in presence of aluminium sulphate and following with a treatment with conc. HCl in order to decompose the Al compound formed. Thus diazotised aniline gave 3:4-dihydroxyazobenzene, whereas in absence of the Al salt only tar resulted. E. S.

History of the Development of the Azoic (Naphtol AS) Dyes. W. Kirst and W. Neumann. *Angew. Chem.*, **66**, 429–434 (1954).

Historical, 58 references. C. O. C.

Reactions with ^{15}N. XV—Reaction of 2-Hydroxy-3-naphthoic Acid with Phenylhydrazine. K. Clusius and M. Barsh. *Helv. Chim. Acta*, **37**, 2013–2018 (Dec. 1954).

The 3:4-benzocarbazole-1-carboxylic acid obtained in 13–14% yield by heating 2-hydroxy-3-naphthoic acid and $^{15}NH_2{\cdot}NH{\cdot}C_6H_5$ up to 150°c. contains a proportion of heavy nitrogen corresponding to a mixed mechanism of formation, 12% of the nitrogen being derived from the marked amino group. H. E. N.

Structures and π-Electron Spectra—Triphenylmethane Dyes. C. E. Looney. *Univ. Microfilms* (Ann Arbor, Mich.) *Publ.* No. 8353, 74 pp. (microfilm $1, paper enlargement $7.40).

Chromatographic Separation of the Aminofluorescein Isomers. J. De Repentigny and A. T. James. *Nature*, **174**, 927–928 (13 Nov. 1954).

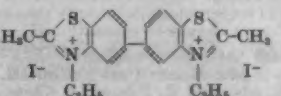
The two isomers of aminofluorescein, which are obtained by condensation of 4-nitrophthalic acid and resorcinol followed by reduction, may be efficiently separated by chromatography on a kieselguhr column (Hyflo-Supercel) using phosphate buffer (pH 8·0) as stationary phase and a mixture of *n*-butanol and *cyclo*hexane as mobile phase. Gradient elution is recommended, starting with 30% (by vol.) *n*-butanol and continuously increasing the butanol concn. Final yields (after recrystallisation) of 23% and 14·3% respectively of the two isomers are obtained, compared with 11·7% and 4% obtained by the method of fractional recrystallisation of the nitrofluorescein diacetates before reduction. A. J.

Reaction between Phthalein Dyes and Heated Foodstuffs. A. Frölich. *Nature*, **174**, 879 (6 Nov. 1954).

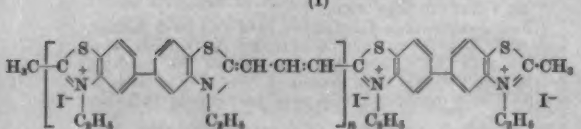
Syntheses of Cyanine Dyes. XX—A New Synthetic Method for a New Type of Trinuclear Trimethin Dyes. Y. Tanabe and M. Yasauda. *J. Pharm. Soc. Japan*, **74**, 814–818 (1954).

Polycondensed Trimethin Dyes. M. Pailer and E. Renner-Kuhn. *Mh. Chem.*, **85**, 601–606 (June 1954).

From 4:4′-dichloro-3:3′-dinitrodiphenyl, (I) was prepared and then condensed with an excess of ethyl orthoformate to give a mixture of substances of formula II. This was resolved chromatographically on alumina, using chloroform with up to 5% alcohol for development. Substances with $n = 2$, 3, and 4 were isolated, λ_{max} being 575, 576, and 575 mμ. respectively; i.e. the absorption was almost identical with that of the simple benzothiazole dye III.



(I)



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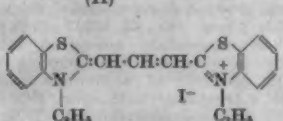


(III)

H. E. N.

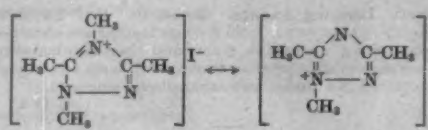
Reaction of 4-Methyl-1-naphthol with Azobenzene and its Bearing on the Chemistry of the Azine Dyes. W. Bradley and L. J. Watkinson. *Chem. and Ind.*, 1482 (27 Nov. 1954).

4-Methyl-1-naphthol when heated with azobenzene yields a dianilinostilbenequinone, and its immediate precursor is presumed to be 4-methyl-1:2-naphthaquinone-2-anil (I); free aniline is always encountered in the reaction. The formation of I is shown, by an example, to bear on the synthesis of those azine dyes which result from the action of azo compounds on amines.

H. H. H.

Structure of Triazole Quaternary Salts. G. F. Duffin, J. D. Kendall, and H. R. J. Waddington. *Chem. and Ind.*, 1458–1459 (20 Nov. 1954).

Data are reported from which it appears that in a 1:2:4-triazole the N-atom which is involved in quaternary salt formation is that in the 4-position, and that the methiodide of 1:3:5-trimethyl-1:2:4-triazole has a structure which can be represented by the canonical states I and II.



(I) (II)

H. H. H.

Blue Phthalocyanine Pigments. V—Intermediates formed during Pigment Formation and Estimation of the Quantities of Gases produced. M. Mori. *J. Chem. Soc. Japan, Ind. Chem. Sectn.*, **56**, 679–681 (1953); **VI—Effects of Various Metallic Compounds as Catalysts.** *Ibid.*, 681–683; **VII—Action of Boric Acid as Catalyst.** *Ibid.*, 768–769; **VIII—Physicochemical Properties of Phthalocyanine Pigments.** *Ibid.*, 769–770: *Chem. Abs.*, **48**, 13235 (10 Nov. 1954).

V—The amounts of CO_2, NH_3, H_2O, pigment, phthalimide, biuret, etc. formed during the production of copper phthalocyanine from phthalic anhydride, urea and $CuCl_2$ using H_3BO_3 as catalyst have been determined, and mechanisms are suggested for the course of the reaction.

VI—When ammonium molybdate, tungstate, or vanadate or $AlCl_3$ is substituted for H_3BO_3 as catalyst in the Wyler method, 30–71% yields are obtained if heating is carried out at 220°c. for 4 hr. The highest yield is obtained when ammonium molybdate (calc. as 2% Mo) is used. The colour of the products did not differ from that got when H_3BO_3 is used.

VII—In the Wyler method the function of the H_3BO_3 seems to be to introduce NH_2 into the phthalic anhydride.

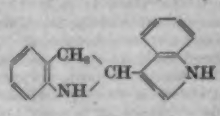
VIII—No difference in the properties of the pigments produced in VI could be observed. C. O. C.

Technology of the Phthalocyanines. I—Their Chemistry. R. E. Brouillard. *Amer. Ink Maker*, 32, (1), 32–35, 65 (1954); **II—Their Application as Pigments.** *Ibid.*, (3), 30–33, 65, 67 (1954): *Chem. Abs.*, **48**, 13236 (10 Nov. 1954).

History and review, 78 references. C. O. C.

Dimerisation and Trimerisation of Indole. G. F. Smith. *Chem. and Ind.*, 1451–1452 (20 Nov. 1954).

Structures I and II are proposed for indole dimer and trimer respectively, since they account for all known reactions and are also supported by a valid mechanistic argument. No plausible mechanism can be formulated for the structures previously proposed by Schmitz-Dumont, Hamann, and Geller (*Liebig's Annalen*, **504**, 1 (1933)).



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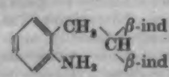
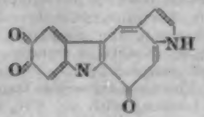


(II)

H. H. H.

Oxidation of 5:6-Dihydroxyindoles, and the Structure of Melanin. J. M. Bruce. *J. Appl. Chem.*, **4**, 469–473 (Sept. 1954).

Quantitative evidence is cited in support of the following series of reactions leading to the formation of melanin from 5:6-dihydroxyindole— A mixture of 5:6-dihydroxy-(3:4′ and 3:7′)-di-indolyl-5′:6′-quinones is first formed. Fission of the *o*-quinonoid rings of these compounds to either a dicarboxylic acid or an *α*-keto acid, followed by recyclisation through the 2-position of the intact indole nucleus, gives, after decarboxylation, a mixture of two *o*-dihydroxy cpd., which, after oxidation to the corresponding *o*-quinones (I and II), undergo oxidative copolymerisation to a substance having the properties of melanin. The application of the hypothesis to substituted 5:6-dihydroxyindoles is described.



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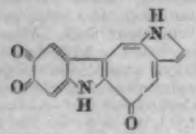


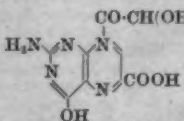
(II)

A. E. S.

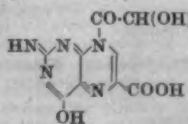
Synthesis of 1-Aza-azulan-2-one and its Electrophilic Substitution; Synthesis of 1-Aza-azulene and its Derivatives. T. Nozoe, S. Seto, S. Matsumura, and T. Terasawa. *Chem. and Ind.*, 1356–1357; 1357–1358 (30 Oct. 1954).

Pteridines from *Drosophila*. I—Isolation of a Yellow Pigment. H. S. Forrest and H. K. Mitchell. *J. Amer. Chem. Soc.*, **76**, 5656–5658 (20 Nov. 1954); **II—Structure of the Yellow Pigment.** *Ibid.*, 5658–5662.

An account of the isolation and purification of a water-soluble yellow pigment from the eyes of two species of *Drosophila* and of work which indicates that the pigment has the structure—



or possibly (as suggested by H. C. S. Wood at the Ciba Conference on the Chemistry and Biology of Pteridines held in London, March 1954)—



C. O. C.

Absorption Spectra of Pyrylium Salts. A. N. Nesmeyanov, L. A. Kazitsyna, N. K. Kochetkov, and M. I. Rybinskaya. *Izvestiya Akad. Nauk S.S.S.R., Otdel. khim. nauk*, 784–795 (Sept.–Oct. 1954).

Absorption spectra are detailed, graphically and in tables, for acetic acid soln. of 13 benzopyrylium (including 9 flavylium) and 10 naphthopyrylium chloroferrates over the range 334–579 mμ. Their relation to the structures of the cpd. is discussed. A. E. S.

Ultramarine Blue. C. A. Kumins. *Amer. Ink Maker*, **32**, (5), 47–49, 51–55, 113 (1954): *Chem. Abs.*, **48**, 13235 (10 Nov. 1954).

Historical, followed by a review of its chemistry and structure, manufacture and properties. C. O. C.

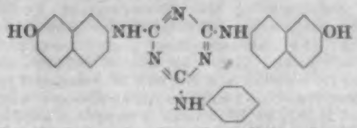
PATENTS

o-Aminophenols—Intermediates for Dyes. Gy. *BP* 720,251

The nuclear bound halogen atom in 4-halogeno-3-nitrophenyl-1-chloromethyl sulphone is readily replaced by the hydroxyl group, without the chloromethyl group being appreciably saponified, by treatment with alkali. The product is then reduced and a good yield of 4-hydroxy-3-aminophenyl-1-chloromethyl sulphone, an intermediate for many dyes, obtained. C. O. C.

Brown Azoic Dyes. FH. *BP* 718,560

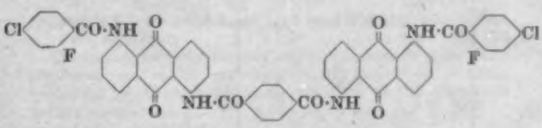
4-Aminodiphenylamine and its substitution products are diazotised and coupled with triazine derivatives of 1:6- or 2:7-aminonaphthol to give brown azoic dyes on cellulosic fibres. The triazine derivatives are made by condensing 1, 2 or 3 mol. of 1:6- or 2:7-aminonaphthol (or their *N*-alkyl, -aralkyl, -aryl, or -*cyclo*-alkyl derivatives) with 1 mol. of a 2:4:6-trihalogenotriazine or a conversion product thereof still containing at least one labile Hal atom. Thus the compound—



with diazotised 4-amino-3-methoxydiphenylamine gives a dark brown. E. S.

Halogenoacylaminoanthraquinones—Vat Dyes. Ciba. *BP* 718,524

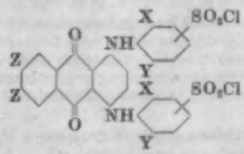
1:5-Diaminoanthraquinone is acylated so that the final product contains at least one benzene nucleus with F *o* to and Cl *p* to the –CO– and may also contain two amino-anthraquinone residues linked by a dicarboxylic structure (cf. *BP* 658,722— J.S.D.C., **68**, 100 (1952)) to give yellow vat dyes. Thus the dye—



is prepared by refluxing 1-amino-5-(4′chloro-2′-fluorobenzoylamino)anthraquinone and terephthalic acid dichloride in trichlorobenzene for 2 hr. R. K. F.

Anthraquinone-1:4-diarylsulphonamides—Acid Dyes. S. *BP* 717,455

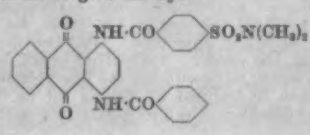
Ammonia or an amine condensed with a sulphonyl chloride of formula—



(X and Y = CH_3 or C_2H_5; Z = H, Cl or Br) yields blue acid dyes fast to milling and light. Thus, a moist paste of 1:4-bis(2′:4′:6′-trimethylphenylamino)anthraquinone-disulphonyl chloride is stirred with an aq. solution of 2-aminoethane sulphonic acid. $NaHCO_3$ and 80% *iso*-propyl alcohol are added and after heating at 50°c. for 3 hr., and then at 80°c. for 2 hr., NaCl is added and the product filtered off. R. K. F.

Acylaminoanthraquinone-Sulphonamides—Intermediates and Vat Dyes. Ciba. *BP* 718,566

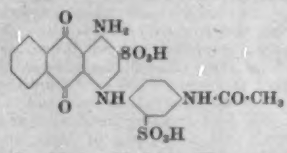
The sulphochloride of an aryl carboxyl chloride is condensed with a vattable amine and the product treated with a primary or secondary non-vattable amine to give vat dyes or intermediates which are convertible into vat dyes. Thus *p*-sulphobenzoyl dichloride is heated at 125–135°c. for 2 hr. with 1-amino-4-benzoylamino-anthraquinone in nitrobenzene. After filtering the product is stirred in pyridine for 6 hr. at 30–35°c. with 30% aq. dimethylamine to give the dye—



R. K. F.

1-Amino-4-phenylamino-2-sulphoanthraquinones Sulphonated in the Phenyl Nucleus— Acid Dyes. S. *BP* 718,885

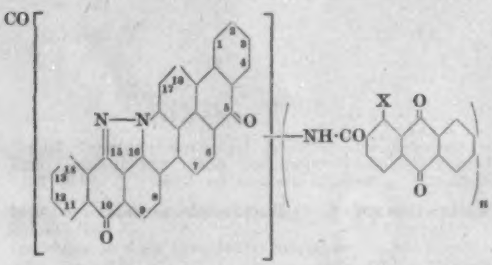
Dyes of the type—



are level-dyeing blue acid dyes. They are made either (i) by sulphonating the corresponding 1-amino-4-(*p*-acylaminophenylamino)-2-sulphoanthraquinone or (ii) by acylating the corresponding *p*-amino-*o*-sulphophenylamino derivative. Thus the dye of formula shown is prepared by treating the Na salt of 1-amino-4-(*p*-acetylaminophenylamino)-2-sulphoanthraquinone with 25% oleum in H_2SO_4 at 40°C. until a sample is soluble in 5% aq. NaCl, after which the whole is run into ice and water containing NaCl. R. K. F.

Benzanthronepyrazoleanthrone Derivatives— Vat Dyes. ICI. *BP* 716,558

A benzanthronepyrazoleanthrone carrying one or two NH_2 groups at 3, 9, 11 or 14 positions is condensed with the halide of a 1-nitro- or 1-aminoanthraquinone-2-carboxylic acid to produce a direct black vat dye of formula—



($X = NO_2$ or NH_2; n = 1 or 2). Thus 11-aminobenzanthronepyrazoleanthrone is heated at 140–145°C. for 18 hr. and at 200–210°C. for 5 hr., with 1-nitroanthraquinone-2-carboxylic acid chloride in nitrobenzene. After filtering off the product is suspended in nitrobenzene at 190–200°C. for 6 hr. while NH_3 is passed through. R. K. F.

Copper Polychloro-phthalocyanine. IC. *BP* 717,783

Equimolecular proportions of 4-chlorophthalic anhydride and a mixture of 3:6-, 4:5-, and 3:5-dichlorophthalic anhydride are heated in trichlorobenzene at 140°C., $CuCl_2$ and ammonium molybdate added, and the whole heated to 190°C. for 2 hr. The product after separating is extracted with alcohol, aq. alkali and acid; it is finally acid-pasted to give a pigment suitable for printing inks. It has the same hue as Peacock Blue pigment, and better fastness to light, heat, acids and alkalis. R. K. F.

Water-soluble Phthalocyanines. FBy. *BP* 717,137

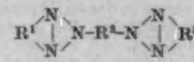
Phthalocyanines are condensed with ω-hydroxy-*N*-methylphthalimide in H_2SO_4 or $AlCl_3$–tertiary amine mixtures and the product hydrolysed with acids to produce water soluble blue to green dyes of formula—

$$Pc\text{-}(CH_2{\cdot}NH_2{\cdot}HX)_n$$

(where Pc = phthalocyanine residue; X = Hal; n = 1–8). They have affinity for wool, tanned cotton and rayon. Thus, ω-chloro-*N*-methylphthalimide and copper phthalocyanine are heated together at 130–140°C. for 3 hr. in a mixture of $AlCl_3$ and piperidine. After pouring on to ice and filtering, the product is dissolved in dil. aq. NaOH, excess HCl added to precipitate the free phthalamic acid, which is then hydrolysed by boiling for ca. 1 hr. The resulting hydrochloride is precipitated by adding NaCl. R. K. F.

Bis-1:2:3-Triazole Derivatives — Fluorescent Brightening Agents. CAC. *BP* 716,338

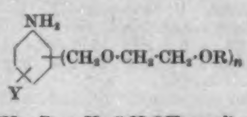
Compounds of formula—



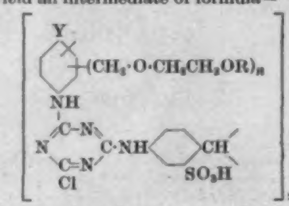
(R^1 and R^3 = naphthalenesulphonic acids linked to the triazole residues at positions 1:2 of the naphthalene nucleus; R^2 = phenylene, to which the triazole rings are linked at *p* positions) are fluorescent brightening agents. The different stages of their synthesis may be carried out in a variety of ways. These consist essentially of first linking one or both naphthylamine sulphonic acids (capable of coupling *o*- to the NH_2) through an azo group to the benzene ring and then oxidising to the corresponding triazole derivative. Thus, *p*-amino acetanilide is diazotised and coupled with 2-aminonaphthalene-3:6-disulphonic acid. After salting out the resulting azo compound is hydrolysed with aq. NaOH to remove the acetyl group, diazotised and coupled with 2-aminonaphthalene-6-sulphonic acid. The disazo dye thus formed is salted out and oxidised by treating with aq. NH_3 and $CuSO_4$ at 75–80°C. The bis-triazole is separated by acidifying and adding NaCl. R. K. F.

Triazine Fluorescent Brightening Agents. General Aniline. *USP* 2,660,578

Fluorescent brightening agents are obtained by condensing 1 mol. of 4:4′-diamino-2:2′-stilbenedisulphonic acid with 2 mol. of cyanuric chloride. The triazyl derivative so produced is then condensed with 2 mol. of a compound of formula—



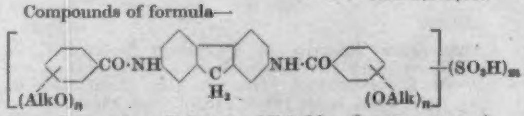
($Y = H$ or CH_3; $R = H$, C_2H_4OH or alkylmethyl; n = 1 or 2) to yield an intermediate of formula—



which is then condensed with > 1 mol. of an amine or organic hydroxy compound. C. O. C.

Diaminofluorene Derivatives— Fluorescent Brightening Agents. American Cyanamid Co. *USP* 2,662,913

Compounds of formula—



(m and n = 1 or 2) have reddish blue fluorescence and affinity for cellulose. C. O. C.

Production of Organic Dyes and Pigments in Finely-divided Form. ICI. *BP* 719,072

Organic colouring matters are produced in a finely-divided form by treating them with a suitable metal halide (or a complex thereof with an organic compound), preferably in presence of a solvent, followed by decomposition of the resulting complex with water. The process is particularly applicable to phthalocyanine pigments. Thus, all parts being by weight, NaCl (3·3) and $AlCl_3$ (7·27) are added to dry ethylene dichloride (120) and heated to 50°C. At 20°C. copper phthalocyanine (25) is added, and the mixture stirred at room temperature for 18 hr. After dilution with water, the solvent is removed by distillation in steam, leaving the pigment in its β-form in a finely-divided state. E. S.

Aluminium Flake for Translucent Metallic or Polychromatic Coatings. DuP. *USP* 2,662,027

Aluminium flake of which $\not> 5\%$ of the total covering area of all flakes is given by flakes having a dimension $> 25\mu$ and $\not> 25\%$ by flakes having a dimension $< 5\mu$, and which has a covering area of 14,500–17,000 sq. cm./g. (determined by the test described by J. D. Edwards in "Aluminum Paint and Powder") used in translucent metallic or polychromatic coating compositions yields coatings clearer, brighter and glossier than if ordinary aluminium flake is used. C. O. C.

Silica Pigment. Wyandotte Chemicals Corpn. *BP* 719,918

Soft impalpable silica suitable as a pigment is produced by mixing an alkali metal halide (15–20 g./litre) with an aqueous solution containing sodium silicate (30–105 g. SiO_2/litre) and an alkali metal halide (15–50 g./litre). Conditions of precipitation should be such that the silica precipitated has average particle size $\not> 1\mu$., after filtering the filter cake contains 78–87% of water and the dried pigment has a packed density $\not> 0{\cdot}23$ g./c.c. C. O. C.

Vat Dyes—A Miscellany (VIII p. 115).

Antidiffusion Diazotypes having Tetrazo Diphenyls as the Light Sensitive Agent (IX p. 117).

Magenta Photographic Images (IX p. 117).

Differences and Analogies between the Chemical Compositions of Synthetic Tanning Agents and Leather Dyes (XII p. 120).

Identification of Di- and Poly-amines and Aminohydroxy Compounds as Fission Products of Azo Dyes. [Constitution of Commercial Azo Dyes] (XIV p. 122).

V—PAINTS; ENAMELS; INKS

Fluidity and Critical Pigment Volume of Industrial Paint Materials. G. Zeidler and G. Eberle. *Kolloid-Z.*, **139**, 115–120 (Nov. 1954).

The fluidity of various agents used in the paint industry is discussed. Non-pigments are characterised according to Leppert and Majewska by reaction with a special wood oil, in which surface tension plays a dominant rôle, and also by absolute viscosity data (including structural viscosity and thixotropy). Experimental work is described for obtaining minimum oil requirements, and for the classification of different pigments for fluidity when admixed with various binding agents. The work of Asbek and Van Loon is quoted for obtaining a critical pigment volume, which is found to be dependent on the acid number and the D.P. of the linseed oil used. The effects of binding agents, pigments, and additions such as suspension promoters, skin protectors, etc. are described. H. H. H.

Linseed Oil at the Surface of Titanium Dioxide Pigment—Study by High-magnification Electron Micrography. W. R. Lasko and L. S. White. *Anal. Chem.*, **26**, 1631–1635 (Oct. 1954).

It has been shown, by a high-magnification electron-microscopic study, that the rough and fuzzy appearance of the edges of particles of pigments arises from the natural roughness of the surface, as well as from the presence of adsorbed oil. In some instances the oil is non-uniformly adsorbed, indicating that the particle surface itself is heterogeneous. There is a difference between unpolymerised and polymerised linseed oil in the nature of the fuzziness at the pigment surface, and also in its extent. There are eight electron micrographs to illustrate the text. J. W. D.

Pigment Studies at National Printing Ink Research Institute. W. C. Walker, A. C. Zettlemoyer, and E. Gamble. *Amer. Ink Maker*, **32**, (5), 56–57, 59, 61, 113 (1954): *Chem. Abs.*, **48**, 13236 (10 Nov. 1954).

Summary of work on behaviour of pigments in printing inks. Most of the effect of pigments on the properties of printing inks is caused by pigment particle–liquid vehicle interfacial phenomena. Loss of drying on ageing and some remedies, dispersion, and surface chemistry measurements are discussed. C. O. C.

Influence of Paper on the Autoxidative Drying of Printing Inks. R. R. Coupe. *J. Oil & Col. Chem. Assocn.*, **37**, 621–637 (Nov. 1954).

The rate of drying of printing ink on paper falls as the acidity of the paper rises, the effect being more marked at higher ambient humidity; this is primarily due to the irreversible sorption of cobalt (probably as the ion) on the cellulose fibres. Difficulty is more often experienced in lithography than in letterpress printing, owing to the larger amount of water, the smaller amount of Co, and the thinner films customary with the former process. Addition of cobalt nitrate to the ink, or to the fountain soln., may afford a remedy. J. W. D.

PATENTS

Glass Staining Compositions. Verd-A-Ray Processing Co. *USP* 2,662,035–7

Combinations of Cu, Ag and Zn salts in presence of the chlorine anion are active staining materials for several types of glass, different colours being obtained according to the type of glass and the proportions of the staining salts. An aqueous dispersion of the salts is applied to the glass which is then heated to 800–1100°F. to produce a stained surface. C. O. C.

Artists' Watercolour Paints. Binney & Smith Co. *USP* 2,662,031

Solid polyethyleneglycol of high mol.wt., e.g. average mol.wt. 4,000–6,000, to which has been added a little of an alcohol, e.g. stearyl alcohol, and an aqueous solution of a polyhydroxy compound, e.g. sorbitol, is an excellent water-soluble, liquefiable vehicle for watercolour paint. C. O. C.

Storable Pigmented Lacquers and Paints. Chemische Werke Albert. *BP* 720,176

Thickening of lacquers and paints pigmented with basic pigments or metal powders is inhibited by adding stabilised aluminium alkoxide solution to the lacquers before pigmentation. C. O. C.

Aluminium Flake for Translucent Metallic or Polychromatic Coatings (IV this page).

National Printing Ink Research Institute Standard Method for Tinting Strength of Printing Ink Pigments (XIV p. 122).

VI—FIBRES; YARNS; FABRICS

Freezing of Swollen Cellulose Fibres. N. I. Klenkova and N. I. Nikitin. *Faserforsch. und Textiltech.*, **5**, 443–446 (Oct. 1954).

A long résumé in German, with tabulated data, of Russian papers already abstracted (J.S.D.C., **70**, 315 (July), 370 (Aug. 1954)). A. E. S.

Structure of Cotton α-Cellulose. D. B. Das, M. K. Mitra, and J. F. Wareham. *Nature*, **174**, 1058–1059 (4 Dec. 1954).

The formic acid hydrolysate of α-cellulose from American and Egyptian cotton gives indications of the presence of xylose and arabinose, in addition to glucose, on a paper chromatogram. The presence of pentoses in the sulphuric acid hydrolysate is also indicated. It is thought that the pentoses are associated closely with cotton α-cellulose (as with jute, etc.), but at present it is difficult to assess the exact amount of pentose. The existence of mixed crystals of pentoses with glucose in cotton α-cellulose is tentatively suggested. A. J.

Degradation of Cellulose by Alkali Cooking. I—Formation of Carboxyl Groups. O. Samuelson and A. Wennerblom. *Svensk Papperstidning*, **57**, 827–830 (30 Nov. 1954).

The degradation of cotton cellulose by alkaline cooking at 170°C. has been investigated, and a comparison of the content of carboxyl groups with the D.P. determined osmotically shows that after degradation the cotton has one –COOH group per chain molecule. For each splitting of a cellulose molecule it follows that there is one –COOH in the chain, apparently as an end-group. From the relationship between yield and –COOH group content of the cellulose it has been calculated that at the beginning of the cook about 50 glucose residues are destroyed and go into solution at every splitting of a cellulose molecule.

The kinetics of the formation of carboxyl groups in cellulose is explained with the aid of a schematic model for the degradation mechanism. S. V. S.

Decrease of Viscosity and Degree of Polymerisation of Cellulose during the Viscose Process. T. Kleinert and V. Mössmer. *Mh. Chem.*, **85**, 627–636 (June 1954).

Two samples of sulphite cellulose of similar cuprammonium viscosity and D.P. were found to be polydisperse in different ways. The alterations in polydispersion on oxidation with cold dil. H_2O_2 (30 : 1, 4 g. per litre) are recorded, the fractions of higher D.P. being diminished first. Eight samples of cellulose from fir or beech were examined for cuprammonium viscosity and D.P. at various stages during the viscose process, the curve relating the two being characteristic of each material. H. E. N.

Interaction of Hair Fibres with Alkali-metal Bromide Solutions. W. S. Barnard, A. Palm, P. B. Stam, D. L. Underwood, and H. J. White. *Text. Research J.*, **24**, 863–881 (Oct. 1954).

The interaction of hair with alkali-metal bromide solutions has been studied by measuring the amount of salt taken up by a radioactive-tracer technique, and the amount of water taken up by a gravimetric technique. The results and their interpretation in terms of various simple models of the absorption process are discussed. A. B.

Fibroin cross-linked with 4:4′-Difluoro-3:3′-dinitrodiphenyl Sulphone. H. Zahn and H. Zuber. *Mh. Chem.*, **85**, 759–778 (Aug. 1954).

Fibroin dissolves in conc. HCl, in cupriethylenediamine, and in aq. LiBr, but when cross-linked with 4:4′-difluoro-3:3′-dinitrodiphenyl sulphone as described previously (*Chem. Ber.*, **86**, 172 (1953)) it is no longer soluble, though it contracts about 60%. This contraction destroys the double refraction and the orientation of the X-ray photograph, but washing and stretching restore both. The cross-links between the chains of fibroin lie in the tyrosine-rich segments. The cross-linked fibroin serves as a model for experiments on the hydrogen-bond-breaking type of supercontraction and resembles native keratin with its disulphide bonds in the cystine-rich segments. Formic acid causes fibroin to swell and contract, but cross-linking largely prevents its action. Fibroin treated with 4-fluoro-3:3′-dinitrodiphenyl sulphone behaves in all respects almost as untreated, being only slightly stabilised. 21 X-ray photographs and 30 references. H. E. N.

Amino Acids in Animal Fibres and Superpolyamides. E. Justin-Mueller. *Teintex*, **19**, 841–843 (Nov. 1954).

Amino acids exist in a preformed state in nylon, but are obtained only after prolonged hydrolysis in the case of wool. Their formation can be followed in the latter instance by the use of copper sulphate or ferric chloride. S. R. C.

Relationship of the Properties of a Polyamide to the Structure of its Repeating Unit. V. V. Korshak and T. M. Frunze. *Doklady Akad. Nauk S.S.S.R.*, **97**, 261–264 (11 July 1954).

The m.p. y (°C.) of a linear polyamide formed by the polycondensation of $NH_2{\cdot}[CH_2]_p{\cdot}COOH$, or of $NH_2{\cdot}[CH_2]_q{\cdot}NH_2$ with $COOH{\cdot}[CH_2]_r{\cdot}COOH$, p, q, and r being even numbers, is practically independent of the arrangement of methylene and amide groups within the repeating unit and is determined essentially by the ratio x (%) of the number of amide groups to the number of methylene groups. For 14 such polyamides, and also for polyethylene ($x = 0$, $y = 110$°C.), the following equation is closely obeyed—

$$y = 7x + 110$$

For such polyamides x is the number of hydrogen bonds formed per unit, every amide group being concerned in hydrogen-bond formation; but in general—

$$y = 7kx + 110$$

k being the fraction of the amide groups that are sterically able to enter into hydrogen-bond formation; the number of hydrogen bonds per repeating unit can therefore be calculated from the m.p. of the polymer. When p is odd, when q and r are odd, and when q or r is odd, $k < 1$ and it varies from 0·49 ($q = 9$, $r = 7$) to 0·94 ($q = 5$, $r = 18$). For mixed polycondensates (e.g. those formed from mixtures of hexamethylenediamine adipate and hexamethylenediamine sebacate), k is again less than unity. A. E. S.

Dichroic Study on Polyvinyl Alcohol Fibre. IV—Theoretical Relation between Intrinsic Double Refraction and Dichroism. Y. Kobayashi and S. Okajima. *Bull. Chem. Soc. Japan*, **27**, 469–471 (Oct. 1954).

A linear relationship is derived between intrinsic double refraction and dichroic orientation. W. R. M.

PATENTS

Water-resistant Protein Materials. Eastman Kodak Co. *USP* 2,663,617

Proteins, especially protein fibres, when acetoacetylated with diketen and then treated with formaldehyde are given good resistance to water, and improved resiliency and handle. C. O. C.

Dyed Aromatic Polyesters. Vereinigte Glanzstoff-Fabriken. *BP* 720,057

A solution of a linear aromatic polyester and an organic dye soluble in both the common solvent and the polyester is coagulated and the precipitated dyed polyester melt spun into fibres. C. O. C.

Stabilising Polyacrylonitrile to Heat. Monsanto. *USP* 2,661,343–7

Al or Mn salts, Ca or Sr compounds, maleic acid and anhydride incorporated into polyacrylonitrile prevent discoloration on heating. C. O. C.

Acrylonitrile Co-polymers. Rhône-Poulenc. *BP* 718,557

Co-polymers of acrylonitrile (5–80%) and a vinyl ether of an amino alcohol (20–95%) which have been prepared in concentrated aqueous solution have a high amino ether content and are readily soluble in dimethyl formamide. Mixtures of these polymers and acrylonitrile have an affinity for acid dyestuffs. W. G. C.

Co-polymers of *N*-Vinyl-substituted Iminazoles. BASF. *BP* 718,673

Co-polymers of acrylonitrile and *N*-vinyl compounds of iminazoles which have a mono-substituted alkyl radical on the C-atom in the 2-position, e.g. methylol, are suitable for spinning into fibres with good affinity for acid and acetate dyestuffs. W. G. C.

Acrylonitrile-Nicotinamide Copolymers. Chemstrand Corpn. *USP* 2,664,412

Compounds of formula—

(R^1 = allyl, methallyl or ethallyl; R^2 = H or Alk of 1–5 C), e.g. *N*-alkylnicotinamide, when copolymerised with acrylonitrile yield a product suitable for forming into fibres which are readily dyed with acid dyes. C. O. C.

Acrylonitrile-Vinylidene Chloride Copolymer Filaments. BrC. *BP* 720,380

An acetone solution of the copolymer is extruded into a coagulating bath containing $\not<$ 83% by wt. of hydrocarbons. C. O. C.

Forming Filaments from Fusible Material. BrC. *BP* 719,853, *BP* 719,860

A method of forming fibres from a powdered fusible filament-forming material, e.g. cellulose acetate, with addition if desired of pigments. C. O. C.

Photochemical Degradation of Untreated and Matt Cellulosic Fibres (X p. 118).
Interaction of Benzyl Acetate and Cellobiose α-Octaacetate with Solvents for Cellulose Acetate (XI p. 119).
Investigation of the Physical Structure of Synthetic Polyamides with the aid of Infrared Absorption Spectra (XIII p. 120).
Equilibration in Molten Polyamide Mixtures (XIII p. 120).

Exchange Reactions between Polyamide Macromolecules (XIII p. 120).

Determination of the Molecular Weight of Polyethylene Terephthalate by End-group Assay (XIII p. 121).

Influence of Chemical Treatment on the Properties of Wool. I— Alkali Solubility as a Measure of Sulphuric Acid Degradation (XIV p. 123).

Textile-shrinkage Control Processes and Test Methods (XIV p. 123).

VII— DESIZING; SCOURING; CARBONISING; BLEACHING

Concentration Dependence of the Electrophoretic Mobility of Soap Micelles. D. Stigter. *Rec. Trav. chim.*, **73**, 771–782 (Sept.–Oct. 1954).

Solubilisation by Potassium Laurate Solutions. S. Spring and E. Howard. *J. Colloid Sci.*, **9**, 371–381 (Oct. 1954).

Studies have been made of the solubilisation of benzene by potassium laurate solutions containing lauric acid, with additions of 1-butanol to improve solubility. Up to a laurate : lauric acid ratio of 4 : 1 solubilisation increases regularly with the concentration of lauric acid, but at ratios less than this lauric acid causes a great reduction in solubilisation and an increase in viscosity, and reduces the influence of butanol. This change is interpreted in terms of a change from a spherical to a rod-like micellar structure. W. R. M.

Physicochemical Studies related to the Rôle of Whiteness-retention Additives in Detergent Action. W. Fong and W. H. Ward. *Text. Research J.*, **24**, 881–889 (Oct. 1954).

The methods of electrophoresis, sedimentation, and adsorption analysis have been used to investigate the mode of action of whiteness-retention additives in decreasing the extent of soil redeposition during laundering. The ionogenic additives are shown to differ from the non-ionic additives in their specific effects on the surface charge of cotton and on the rate of sedimentation of carbon black, and in their adsorption on cotton. It is concluded that their modes of action in preventing soil redeposition are different. A. B.

Recent Developments in Chlorite Bleaching. P. Mosse. *Teintex*, **19**, 811–838 (Nov. 1954).

The use of esters, e.g. ethyl lactate, is discussed, and the influences of liquor ratio, pH, time, and temperature are examined. The effects of the process on stainless steel and aluminium are described. 86 references. S. R. C.

PATENTS

Bleaching Cellulose. Deutsche Gold- und Silber-Scheideanstalt vormals Roessler. *BP* 718,563

The material is treated with aqueous sodium chlorite, preferably 0·5–10·0 g. per litre, at pH $\nless$ 7, excess liquor removed and the material dried at 80–95°c. if desired after being stood for some time but without being rinsed. C. O. C.

Bleaching Cellulose Derivatives. Hercules Powder Co. *USP* 2,662,884

Cellulose ethers are bleached by forcing them into a slurry with an inert nonsolvent and then treating with a chlorite. C. O. C.

Dry Cleaning. M. Blau. *BP* 719,114

The fabric to be dry cleaned is first momentarily exposed to high pressure steam preferably on a horizontal screen conveyor. The steamed fabric, preferably while still on the conveyor, is pressure sprayed on both sides with an organic detergent and emulsifier, the time of exposure to this spray also being very brief, e.g. for a fraction of a second. Both sides of the fabric are then sprayed with a dry cleaning solvent to remove the emulsified material, including the dirt, from the fabric which is finally dried in the usual manner. C. O. C.

Shrinkage of Cotton Fabric (X p. 118).

VIII— DYEING

Historical Notes on the Wet-processing Industry. VI— The Dual Life of Edward Bancroft. S. M. Edelstein. *Amer. Dyestuff Rep.*, 712–713, 735 (25 Oct. 1954).

Principles of Continuous Dyeing. E. R. Wiltshire. *Textile Digest*, **15**, 254–267 (April–June 1954).

A review of the development of continuous dyeing methods. Recent work on padding and high-temperature fixation is dealt with in detail. A. J.

Effect of Formaldehyde in the Azoic Dyeing of Polyamides and Acetate Rayon. R. Löwenfeld. *Melliand Textilber.*, **35**, 1121–1123 (Oct. 1954).

Although an effective antioxidant in cotton dyeing, formaldehyde interferes with coupling power on hydrophobic man-made fibres, owing to the formation of methylene bridges between two molecules of the coupling component. S. R. C.

Vat Dyes— A Miscellany. M. R. Fox. *Amer. Dyestuff Rep.*, 43, P 730–P 732 (25 Oct. 1954).

The chemical structures of some vat dyes are discussed in the light of reducing, dyeing, and fastness behaviour. J. W. B.

Vat Dyeing of Knit Goods. R. D. Blum. *Amer. Dyestuff Rep.*, 43, P 719–P 725 (25 Oct. 1954).

General methods for vat-dyeing mercerised and unmercerised cotton knit fabrics, in which sodium hydrosulphite is replaced by sodium formaldehyde-sulphoxylate as the primary reducing agent, are detailed and discussed, with regard to both cotton and the newer synthetic fibres. The following advantages in batch-type processing are recorded— controlled rate of exhaustion, giving more level and better penetrated dyeings; increased stability of vat dyes at elevated temperatures, giving brighter colours and better matches; increased stability of the reducing agent; it permits overdyeing of vat and azoic stripes and patterns without affecting the base shades; and there are promising possibilities in dyeing synthetic fibres, including Dacron, dynel, nylon, Acrilan, Orlon 42, cellulose acetate, and blends of these with cotton, at 212°F. by means of pH control during reduction and dyeing. The principal disadvantage encountered is the problem of dispersibility of the dyes as supplied by the various manufacturers. The ideal conditions for sulphoxylate reduction depend upon good dye dispersion, and the ideal dispersing agent for all dyes has not been found. Owing to interfering agents in various dyes as marketed, it might be difficult to find any one agent which will be universally good. J. W. B.

Behaviour of Leuco Vat Dyes above 100°c. S. Blackburn and M. R. Fox. J.S.D.C., **71**, 80–89 (Feb. 1955).

This preliminary study of the behaviour of vat dyes at high temperatures has included examination of the stability of these colouring matters, and some consideration has been given to the use of leuco-dye damage-inhibitors. A number of dyes stable at high temperatures are available, but known leuco-dye protective agents hold out little hope of extending the range to any great extent for the recently introduced package-dyeing systems. Examination of the behaviour of vat dyes over a wide range of temperatures and of their rate-of-dyeing curves has led to the development of a cooling-bath process for the dyeing of cellulosic yarn packages. Improved migration, penetration, and level-dyeing behaviour are features of high-temperature dyeing; dyeing times may be shortened, and the process should prove to be attractive for dyeing tightly twisted mercerised cotton yarns and similar textiles. AUTHORS

Interesting Points in Woollen and Worsted Dyeing and Finishing. G. K. Seddon. *J. Bradford Textile Soc.*, 99–105 (1953–1954).

A brief review from the practical standpoint of crabbing, scouring, dyeing, and finishing is followed by an account of commonly occurring damages and stains caused by manufacturing faults, e.g. leaving a needle in the goods, presence of section marks and wrong ends, etc. Many piece-dyed woollens have to be carbonised, and of these about 8% have to be redyed. Of those carbonised before dyeing, 6% are spoiled and have to be redyed black. Of those carbonised after dyeing, 4% are spoiled and have to be redyed. C. O. C.

Dyeing of Wool at High Temperatures. F. Thies. *Textile J. of Australia*, **29**, 750–763 (Aug. 1954).

Wool can be dyed successfully in appreciably shorter times than normal by the use of high temp.–pressure systems, but care is essential to avoid damage to the fibre. Investigations by the Bayer Co. are described, and wet tensile strengths show that when dyeing wool at pH 5 the same degree of fibre degradation is obtained at 98°C. for 60 min. as at 105°C. for 25 min. and at 110°C. for 17 min. Above 110°C. fibre damage increases very rapidly with rise in dyeing temp., and this is very marked even at 115°C. For bulk application, temp. of 105–107°C. are recommended. On the whole, dyes tend to level better at high temp., but this depends on their migration properties. Rate of dyeing at high temp. can be controlled by careful heating up of the dyebath or the addition of suitable retarding agents. B. K.

Gas Fume Fault on Wool. C. L. Bird. J.S.D.C., **71**, 46 (Jan. 1955).

The colour of an all-wool worsted dyed with a level-dyeing mixture of azo yellow, azo red, and anthraquinonoid blue acid dyes changed from dull blue–green to drab or khaki on storage in a room heated by gas radiators. On filter paper blue anthraquinonoid dyes are very sensitive to nitrous fumes, the greener types appearing to be more sensitive than the common Blue B type (*C.I.* 1054). C. J. W. H.

Some Problems in Dyeing Mixed Fibres. B. Kramrisch. *Text. Manuf.*, **80**, 593–594 (Nov. 1954).

Mixtures of Orlon 42 and cellulosic fibres are dyed solid by the one-bath process with selected disperse (Cibacet) and direct dyes, or with selected basic or modified basic (Diorlene) (Ciba) dyes, to give minimum staining of the cellulosic fibre, together with direct dyes applied by a two-bath process. With unions of Orlon 42 and wool, disperse and most basic dyes give heavy coloration of the wool of poor fastness to light and wet processes. Selected basic or Diorlene dyes giving minimum staining of the wool can be used, however, and the wool cross-dyed with wool dyes from a neutral or weakly acid dyebath. B. K.

Dyeing Wool and Wool–Synthetic-fibre Blends. H. D. Grimes. *Canadian Textile J.*, **71**, 67–71 (5 Nov. 1954).

In the wet finishing of blends of wool and synthetics, the wool usually rises to the surface. Therefore it is liable to rub off first during wear, and care must be taken to ensure perfect solidity in shade between the two fibres to avoid an unsatisfactory appearance of the garment after wear. *Wool–Dacron*: Dyed with wool dyes and selected disperse dyes which give minimum staining of wool using *o*-phenylphenol as carrier. Disperse dyes tend to sublime if subjected to high temp.; therefore care must be taken during processing such as tailor's pressing to avoid marking-off on to white materials. *Wool–Orlon 42*: Solid shades are obtained with wool dyes and selected basic dyes, but cross-staining of the wool by the latter may take place. *Wool–Acrilan*: Solid shades are obtained by first dyeing the Acrilan with disperse dyes at pH 8 using disodium hydrogen phosphate, washing off, clearing the wool if necessary with a detergent, and then cross-dyeing the wool with acid- or neutral-dyeing wool dyes. Reservation of the Acrilan is obtained by pretreatment with Nylon Resist Salt GDC, and the wool is dyed with wool dyes applied with ammonium acetate or metallised dyes applied with 5% formic acid. *Wool–Vicara*: Solid shades are obtained with acid dyes of good migrating properties applied with formic acid at pH 2·5–3·5 or with metallised dyes applied with sulphuric acid. A limited range of chrome dyes can be used, but full chroming is necessary. *Wool–Dynel*: Solid shades are obtained with metal-complex dyes for light and medium shades, and disperse dyes with wool dyes for full shades. Disperse dyes should be selected which show minimum staining of wool, and this can be reduced by the addition of Peregal TW. Aftertreatment with a synthetic detergent assists the removal of loose disperse dye, and therefore tends to improve rubbing fastness. B. K.

Dyeing of Polyacrylonitrile Fibres— Present State of Development. W. Happe. *Rayonne*, **10**, 29–36 (Nov. 1954).

A review. The dyeing of the polyacrylonitrile fibre Pan with various classes of dyes is outlined. Disperse dyes may be applied near the boil, with the aid of swelling agents such as aniline, anthranilic acid, or cresol, or, with better fixation, under pressure without the aid of a swelling agent. Alternatively, the dye may be applied by padding, drying, and then either pressure steaming or exposing to a temp. of 180–240°C. (Thermosol process). Certain vat dyes, especially those of the indigo and thioindigo types, give dyeings of good fastness when applied near the boil; oxidation is best carried out at 85–90°C. Numerous acid wool dyes are marketed as being suitable for Pan; the Roracyl (DuP) dyes are used in high concn., being applied by the cuprous ion method (which is discussed). Happe and Hensel (*Reyon, Zellwolle*, **12**, 1 (1953)) confirm the view that when Pan is treated, during dyeing, with a halogenated ester and Zn powder, enhanced dyeing follows a reaction of the Reformatsky type; there is direct analogy with the cuprous ion process. Basic dyes such as Basic Red and Basic Blue (DuP), the Acrylosols (G), and the Astrazon (FBy) dyes give dyeings up to 2% in strength, which are of notable fastness, especially on Orlon 42. In general, pale shades are best produced by means of disperse dyes, and deep shades with basic dyes (under pressure) or acid dyes (cuprous ion method). The fastness of the dyeings must be determined, since there is often no relation to the fastness of the same dyes on other fibres. A method is given for the dyeing of wool–Pan mixtures.

The affinity of Pan fibres may be improved by copolymerisation— (i) with vinyl esters, followed by treatment with an amine (to improve affinity for acid dyes); (ii) with chlorine-containing vinyl units, followed by treatment with thiourea (giving enhanced affinity for acid dyes); (iii) with vinylpyrrolidone, to give affinity for acid dyes; or (iv) with vinylpyridine. The copolymers tend to yellow in sunlight, and there is also a certain loss of physical properties; the second component is thus limited to 8%, and this also prevents loss of solubility in dimethylformamide. In the dyeing of Pan, especially to deep shades, it is necessary to use pressure, or swelling agents (which are frequently toxic); the cuprous ion method is difficult and complex in practice. There is as yet no satisfactory method for dyeing Pan. J. W. D.

Surface-active Agents in Fur Dyeing. G. Blancher. *Bull. Assocn. Française Chim. Cuir*, **16**, 158–162 (Sept.–Oct. 1954).

Anionic softening agents help to control preliminary alkaline treatments intended to increase, and to improve the evenness of, affinity of fur keratin. Although non-ionic agents have been proposed for the removal and dispersion of fats, waxes, and insol. soaps, which might affect the evenness of uptake of mordants, they do not seem to have been adopted in practice. Oxidative bleaching agents may damage the fur, especially in the presence of iron mordants; many surfactants, including anion-active softeners, have a protective action. In the application of oxidation dyes, surface-active agents may be used to protect or to soften the fur, to control the dyeing process itself, or to disperse the dyes, or metal soaps. Any of these effects may be accentuated by the appropriate choice of surfactant(s). Such agents are equally useful in the application of vegetable dyes such as logwood. The solidity of aniline black dyeings on rabbit furs is improved by the use of cation-active agents; there is some difficulty in avoiding the formation of red or green tints when the dye is used for tipping. Anionic or non-ionic dispersions of waxes may be used to produce printed reserves prior to dyeing, and may subsequently be removed. The penetration of dye soln. used in tipping, tinting, and shading, may be controlled by the use of anionic dispersants or softeners; some of these effects are discussed. In the production of pale or medium shades on sheep or rabbit fur, acetoquinone dyes are pasted with anionic wetting agents, and are strained before use; it is essential that the fur is thoroughly clean. Certain acid and direct dyes are taken up by the leather of chrome-tanned rabbit or sheep skins, leaving the fur almost undyed; the balance may be improved by reducing the affinity of the leather with a condensation product, e.g.

of naphthalene. Urea–formaldehyde resins, or cation-active agents such as octadecylmethylenepyridinium acetate, may be used to waterproof furs. Vat dyes are little used on furs, since there is risk of damage under the alkaline conditions of the vat; the same protective agents which are effective in the bleaching process (see above) are also useful in this connection. The use of surfactants in the post-dyeing operations of washing, dressing, and brightening is discussed briefly. J. W. D.

Effect of Auxiliary and Dressing Agents on the Dyeing of Skins for the Velvet and Glove Trades. C. Faure and H. Poinsard. *Bull. Assocn. Française Chim. Cuir*, **16**, 141–149 (Sept.–Oct. 1954).

The constituents of dressings applied prior to the dyeing of leather are briefly reviewed under these headings: (i) non-ionic substances— fish and animal oils, and surfactants; (ii) anionic softening and emulsifying agents; (iii) cationic agents— quaternary ammonium cpd., which are especially useful at low pH, and where tannage and dressing are carried out simultaneously. Anionic agents reduce the uptake of direct and acid dyes, especially those of small mol. size; the effect is more marked as the number of sulpho groups in the dye mol. increases. The usefulness of anionic agents is thus limited where deep shades such as black and navy blue are concerned. The affinity for basic dyes is enhanced, the agent probably acting as a mordant. Cationic agents decrease the uptake of basic dyes (which, on chrome leather, is already very small), but increase that of acid and direct dyes, at the expense of penetration. This is useful with medium and deep shades, but detrimental in the case of pale shades, with which uniformity of uptake is essential. With velvets there is the further limitation that good dye penetration is necessary to good milling fastness. Non-ionic agents are the most satisfactory; medium and deep shades may be produced under favourable conditions, without reducing the affinity for acid and direct dyes, and without adversely affecting the evenness of uptake, and the penetration of basic dyes. The mechanisms of these effects are discussed, with specific examples. J. W. D.

PATENTS

Colouring Hydrophobic Fibres. DuP. *USP* 2,663,612

The goods are padded or printed with an aqueous solution or suspension of the colouring material, dried and then baked for a brief period, usually at 180–230°C. for < 1 min. Level dyeings or prints of greater depth, fastness to rubbing and washing and, in the case of some fibres, particularly polyethylene polyterephthalate fibre, fastness to light, are obtained than are obtained by conventional dyeing or printing.

USP 2,663,613

When nylon is being treated by the above method it is possible to prolong baking for 2–3 min. This results in speedier fixation of the colour and with some dyes, especially acid dyes, the dyeings are much more level than if a conventional dyeing method is used. The method is particularly suitable for use in continuous dyeing. C. O. C.

Dyeing Polyacrylonitrile. American Cyanamid Co. *BP* 719,087

Organic compounds having all their C atoms in aliphatic (including aryl substituted aliphatic) and/or heterocyclic groups and containing at least one radical of formula NR^1R^2 (R^1 and R^2 = H or aliphatic or together with the N atom = a heterocyclic radical), e.g. diethylene triamine, are excellent assistants when dyeing polyacrylonitrile with vat, acid, direct or azoic dyes. C. O. C.

Bis-1:2:3-Triazole Derivatives— Fluorescent Brightening Agents (IV p. 112).
Simultaneous Drumming and Vacuum Treatment of Skins— Leather Dyeing (XII p. 120).

IX— PRINTING

Fibre Damage in Discharge Printing. H. Rath and J. Rau. *Melliand Textilber.*, **35**, 1125–1130 (Oct. 1954).

Damage occurs in cellulosic fibres printed with formaldehyde-sulphoxylate by the action of moisture during storage before or after steaming, especially at high temperatures. This appears to be due to oxidation, particularly in presence of metallic catalysts, but not with titanium dioxide. Hydrolysis of the fibre can also occur with "neutral" discharge. The defect can be prevented by the use of an antioxidant in alkaline discharges, with the further addition of an acid-binding agent in "neutral" discharges. Also, the printed goods should be stored for short periods only. S. R. C.

PATENTS

Pigment Printing Emulsions. Sun Chemical Corpn. *USP* 2,663,696

Pigmented water-in-oil emulsions whose aqueous phase is a synthetic thermoplastic resinous latex and whose oil phase is a solution of a thermosetting resin in an organic solvent which is a non-solvent for the first resin, yield prints which do not affect the handle of the fabric and which have good fastness to dry cleaning. C. O. C.

Moisture-proof Finishes, Prints, etc. on Textiles. BASF. *BP* 719,683

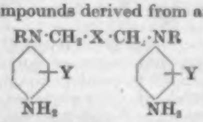
Finishes, pigment prints and dyeings, etc. which are especially fast to rubbing, supple and of excellent fastness to crushing are obtained by use of aqueous dispersions containing as the binding agents polymers containing halogen atoms and acid amide groups, e.g. a vinyl chloride in acrylic acid amide copolymer, and a precondensate of a thermosetting resin, e.g. a urea–formaldehyde precondensate, and a catalyst, e.g. an acid. C. O. C.

Discharges with Thiourea Dioxide on Protein and Cellulose Ester Textiles. Hardman & Holden. *BP* 719,089

When using thiourea dioxide in discharge pastes much whiter discharges are obtained if a zinc salt of an acid which does not discharge dischargeable dyes (e.g. $ZnSO_4$) is added to the paste. Such discharge pastes are very stable but at 100°C. it seems that a compound is formed between the thiourea dioxide and the zinc salt which has a more powerful reducing action than thiourea dioxide alone. C. O. C.

Antidiffusion Diazotypes having Tetrazo Diphenyls as the Light Sensitive Agent. General Aniline. *USP* 2,661,291

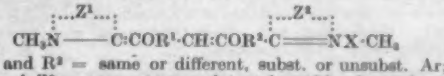
The tetrazo compounds derived from amines of formula



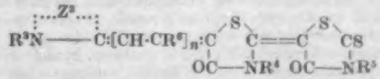
(R = H, Alk or hydroxyl; X = $(CH_2)_m$, $(CH_2)_n \cdot O \cdot (CH_2)_n$ $(CH_2)_n \cdot CHOH \cdot (CH_2)_n$ or $(CH_2)_n \cdot NAlk \cdot (CH_2)_n$ (m = 0–8; n = 0–4); Y = H or Alk) are extremely sensitive to light, have acceptable coupling activities and produce dyes of deep colour having excellent wash fastness. They are fast to precoupling and diffusion and produce dyes of good fastness to diffusion and bleeding in presence of excessive heat or moisture. C. O. C.

A Mixture of Diaryloxythiacarbocyanine and *mero*-Cyanine Dyes as a Photographic Supersensitiser. Kodak. *BP* 718,867

A mixture of a dye of formula—



(R^1 and R^2 = same or different, subst. or unsubst. Ar; Z^1 and Z^2 = atoms to complete a benzthiazole nucleus; X = anion) and one of formula—



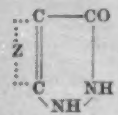
(R^3, R^4 and R^5 = same or different, subst. or unsubst. Alk; R^6 = H, Alk or Ar; n = 0 or 1; Z^3 = atoms to complete a benzthiazole, α- or β-naphthathiazole, benzoxazole or quinoline nucleus) is used as a photographic supersensitiser. C. O. C.

Magenta Photographic Images. Gevaert. *BP* 720,284

Modification of *BP* 663,190 (J.S.D.C., **68**, 98 (1952)).

Dye images of the same structure as obtained by the process described in the parent specification, are produced

by developing a reducible silver salt image with a primary aromatic developer in presence of a compound of formula



(Z= atoms to complete an iso- or heterocyclic or polycyclic nucleus; one or both of the H atoms are substituted by an acyl group) or a tautomer of such a compound. C. O. C.

Heat-sensitive Copying Paper. Minnesota Mining & Manufacturing Co. *USP* 2,663,654–7

The paper is coated with a composition containing components which on irradiation with radiant energy are potentially chemically capable of irreversibly and rapidly reacting at normal room temperature to produce a visibly different reaction product but which are normally physically preserved from so reacting. The composition is so designed that increase in temperature to a predetermined level allows the reaction to occur. Thus a mixture of ferric stearate, hexamethylenetetramine pyrogallate, and oxalic acid with polyvinyl butyral as binder yields a transparent coating which rapidly darkens when heated to 80°c. Paper so coated is suitable for use as a temperature-sensitive copying paper. C. O. C.

Transfer Paper. Standard Register Co. *USP* 2,663,653

The base paper is coated with a colourless or light coloured composition containing a water-soluble Pb, Ag, Bi or stannous compound and a water-soluble polyvalent metal salt of a higher fatty, naphthenic or resin acid. This coating when transferred to another sheet of paper, e.g. by writing on it, becomes black when exposed to dry H_2S. C. O. C.

Colouring Hydrophobic Fibres (VIII p. 117).

X—SIZING AND FINISHING

Photochemical Degradation of Untreated and Matt Cellulosic Fibres—I. A. Agster. *Melliand Textilber.*, **35**, 1209–1212 (Nov. 1954).

Degradation was measured in terms of tensile strength, abrasion resistance, and degree of polymerisation. Iron and copper were found to catalyse the process, but when they were insolubilised or complexed the effect was reduced. Titanium was found noticeably to reduce the D.P. of the exposed bright viscose rayon. An explanation is put forward based on the formation of a cellulose peroxide. S. R. C.

Mechanical and Chemical Dimensional Stabilisation of Textiles. H. Gensel. *Melliand Textilber.*, **35**, 1130–1134 (Oct.), 1260–1262 (Nov. 1954).

A short review. Sanforising, Monforising, overfeeding, and the Haas short-loop dryer are discussed. S. R. C.

Shrinkage of Cotton Fabric. H.-J. Reese. *Textil.-Praxis*, **9**, 1068–1072 (Nov. 1954).

Laundering shrinkage of cotton fabrics can be overcome by (i) mechanical or physical treatment, (ii) by synthetic-resin or chemical finishing, or by combinations of (i) and (ii). Sanforising and other treatments are discussed briefly under these headings. S. R. C.

Shrinkage Control and Durability of Finish. J. A. Woodruff. *Text. Manuf.*, **80**, 587–592 (Nov. 1954).

Good shrinkage control of rayons and rayon blends is produced in America by the Avcoset process, using the following base formula— 1% Avcoset WS (cellulose ether), 10% formaldehyde (37%), 2% sodium bisulphate, and 0·5% sodium suphate made up to volume with water. Quantities used vary with the finish desired and the goods processed and additives such as lubricants, e.g. Avcosol 20 (polyoxyethylene monosorbitan laurate— Atlas Powder Co.) and colloidal silica (to give a dry handle) may be included. B. K.

Wool, Kings, and Parliaments. J. La Page. *J. Bradford Textile Soc.*, 74–80 (1953–1954).

Historical, with references to tentering frauds in the 13th and 16th centuries. C. O. C.

Mechanisms of some Reactions between N-Halogenoamines and Wool. C. Earland. J.S.D.C., **71**, 89–96 (Feb. 1955).

It is shown that the reactions occurring between wool and *N*-halogenoamines do not proceed by common mechanisms. Although these reactions are complex, it is concluded that—

(*a*) *N*-Chlorourea diffuses into the fibre, where the chlorine produced by the equilibrium—

$$NH_2{\cdot}CO{\cdot}NHCl + H^+ + Cl^- \rightleftharpoons NH_2{\cdot}CO{\cdot}NH_2 + Cl_2$$

reacts with the keratin. This explains why the properties of the wool after reaction with *N*-chlorourea differ from those of wool which has been treated with chlorine in acid solution, since under the latter conditions reaction proceeds from the outside to the interior of the fibre.

(*b*) It has been shown previously that *N*-chlorosulphamic acid enters into reactions with wool in acid solution, although reactions that confer unshrinkability occur only in presence of chloride ions at high concentration. Kinetic studies indicate that the rate-determining step in these reactions is the ion-exchange process that determines the rate of access of the *N*-chlorosulphamic acid to the wool. The overall rate of the reactions occurring is accordingly reduced by increasing the concentration of anions, including chloride ions, in the solution. Examination of a number of anions, other than chloride, as possible promoters for the anti-shrink reaction indicates that nitrate also is a promoter, though much less effective than chloride.

(*c*) The high concentrations of free bromine which are produced when solutions of *N*-bromoacetamide and *N*-bromosuccinimide react with wool show that these reactions are essentially brominations. In the initial stages direct reaction between the bromamines and wool is possible, the rate-controlling factor being a diffusion process. AUTHOR

Mothproofing Wool with DDT. A. S. Weatherburn and C. H. Bayley. *Soap & Chem. Specialties*, **30**, (9), 141–144, 163, 165, 167 (1954): *Chem. Abs.*, **48**, 13153 (10 Nov. 1954).

When wool is worked in dil. aq. emulsions of DDT there is rapid pick-up of the DDT out of the emulsion. Presence of detergent in the bath hastens take-up of DDT. The DDT in treated wool is readily removed in subsequent washing with a detergent, so there can be no build-up of DDT by repeated treatments; water alone does not remove DDT. When DDT (0·3% on wt. of wool) was applied in the laundry in the second rinse after a soap wash, the wool contained 0·15% DDT. In a commercial laundry use of 0·8% on the load of work of a commercial insecticidal spray containing 25% DDT imparted an adequate mothproof. C. O. C.

Improvement of Silk Fibres by Chemical Treatments. II—Treatment of Silk Fibroin Fibres with Tetramethylene Diisocyanate. T. Kuwamura and M. Negishi. *J. Chem. Soc. Japan, Ind. Chem. Sectn.*, **56**, 788–790 (1953); **III—Treatment of Silk Fibroin and Raw Silk Fibres with Several Diisocyanates.** *Ibid.*, 790–792: *Chem. Abs.*, **48**, 13225 (10 Nov. 1954).

II—The fibres were swollen successively in 60% methyl alcohol, absolute methyl alcohol, ethyl alcohol, and benzene. They were then treated in a 2·5–10·0% soln. of tetramethylene di*iso*cyanate in benzene or xylene in a sealed vessel for 1–20 hr. at 20–100°c. The treated fibres were washed in benzene and acetone and dried. Tensile strength and elongation at break increased by 15%; there was no improvement in resistance to abrasion, chemicals, or moisture.

III—The fibres were similarly treated with ethylene di*iso*cyanate, octamethylene di*iso*cyanate, *p*-phenylene di*iso*cyanate, methyl *iso*cyanate, dodecyl *iso*cyanate, and octadecyl *iso*cyanate. Treatment with *iso*cyanates containing a long C chain resulted in noticeable improvement in mechanical properties and especially in water-repellency. C. O. C.

Liberation of Formaldehyde during the Storage of Melamine-finished Goods. W. Pässler and H. A. Wannow. *Melliand Textilber.*, **35**, 1134–1137 (Oct. 1954).

With unwashed melamine finishes, more formaldehyde is split off with (*a*) increasing hydroxymethylation of the

resin, (b) increasingly humid storage, and (c) lower baking temp. Urea is a useful formaldehyde acceptor for inclusion in the finish. S. R. C.

PATENTS

Applying Solids or Liquids to Loose Fibres. Chicopee Manufacturing Corpn. *BP* 719,091

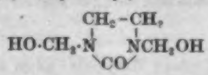
The loose fibres are treated with the solid or liquid which has been converted into an aerosol 95% of the mass of whose particles are $\not> 30\mu$. C. O. C.

Colloidal Methyl Ethers of Methylolmelamine as Textile Finishes. Monsanto. *USP* 2,661,262

Dimensional stability and durable stiffness is imparted to cellulosic fabrics by treating them with an acidic aqueous colloidal solution of incompletely polymerised methylated melamine–formaldehyde or methyl ether of methylolmelamine (combined HCHO:melamine $\nless$ 2·3:1) drying and baking. If the condensate is exhausted on to the fabric then the baking may be omitted. C. O. C.

Imparting Crease-resistance and Stiffness to Textiles. DuP. *USP* 2,661,312

The material is treated with a composition comprising starch, 1:3-bis-(hydroxymethyl)-2-imidazoline



(obtained by treating ethyleneurea with HCHO), an acid catalyst and water, dried and baked. The compositions can be boiled for several hours without change in viscosity. C. O. C.

Shrink-resisting Finish for Fabrics containing Wool. Monsanto. *USP* 2,661, 313

The fabric is first impregnated with a dilute acidic aqueous solution of an incompletely polymerised methylated methylol melamine or methyl ether of a methylol melamine condensate (combined HCHO: melamine $\nless$ 2·3:1) so as to deposit 3·5–8·0% by weight of the condensate on the fabric and is then dried and heated to cure the resin, e.g. 10 min. at 250°F. C. O. C.

Rendering Cellulose Esters Flame- and Glow-resistant. Celanese Corpn. of America. *USP* 2,662,834

Treatment with brominated monomeric triallyl phosphate is used. For materials not to be laundered or dry cleaned, 2–5% suffices, but where permanent fastness to washing and dry cleaning is desired 15–50% should be used. The degree of bromination may be 50–100% of theoretical; best results with respect to washing and dry cleaning being obtained with the fully brominated substance, viz. tri-(2:3-dibromopropyl) phosphate. The treatment does not interfere with either the handle or the dyeing properties of the cellulose ester. C. O. C.

Continuously Embossing Fabrics or Sheets of Synthetic Thermoplastic Material. H. Hiedemann. *BP* 719,964

The material is hung over or below the gap formed by a horizontal pair of embossing rollers and is passed between them in absence of tension. While it is hanging it is heated on one or both sides to render it amenable to embossing when passing through the gap. C. O. C.

Laminated Fabrics. Industrial Accountancy Partnership. *BP* 719,614

To prevent stretching or distortion of the loosely woven cotton–acetate rayon interlining used in the production of laminated fabrics, it is treated with an aqueous dispersion of a thermoplastic resin of softening point 40–130°C. (determined by the ring and ball methods, *Handbook of Plastics* (1949) 1093), so as to deposit 2–5% by wt. of the resin on the interlining. C. O. C.

Cloth of Reduced Infra-red Transmission. American Cyanamid Co. *BP* 718,533

The infra-red transmission properties of cloth are reduced by cementing a leafing metallic powder to it by an alkyd plasticised etherified aminoplast resin. C. O. C.

Imparting Dimensional Stability to Tubular Knitted Fabric. Proctor & Schwartz. *USP* 2,661,520

The moist or wet fabric is stretched widthways in absence of lengthways tension and is then agitated in absence of all tension while being dried and is finally calendered to the desired finished width. C. O. C.

Water-repellent Finish on Natural and Synthetic Textiles. Harris Research Laboratories. *USP* 2,662,039

The fabric is treated with an aqueous emulsion of a silicone oil, dried, and baked. C. O. C.

Coated Knit Fabric. T. A. Clayton. *BP* 718,406

A stretchable, elastic upholstery fabric made by bonding a thermoplastic vinyl resin film to one face of a tightly knitted fabric without filling the interstices. The fabric of plain knit type composed of cotton, rayon or synthetic fibre is knitted to the specified requirements. G. E. K.

Applying Liquids to Slivers, etc. (I p. 107).
Linseed Oil at the Surface of Titanium Dioxide Pigment—Study by High-magnification Electron Micrography (V p. 113).
Interesting Points in Woollen and Worsted Dyeing and Finishing (VIII p. 115).
Moisture-proof Finishes, Prints, etc. on Textiles (IX p. 117).
Textile-shrinkage Control Processes and Test Methods (XIV p. 123).

XI—PAPER AND OTHER CELLULOSIC PRODUCTS

Some Optical Properties of Cellulose Hydrate. S. Okajima, Y. Kobayashi, and T. Kikuchi. *Bull. Chem. Soc. Japan*, **27**, 471–475 (Oct. 1954).

Measurements of the intrinsic double refraction and dichroic orientation of stretched and relaxed isotropic cellulose filaments, obtained by regeneration from cuprammonium soln. and dyed with Congo Red, show a linear relationship between these quantities. The slope of the line is increased by mercerisation and by stretching, and decreased by decoppering. Changes in slope are related to changes in crystallinity and intrinsic double refraction. W. R. M.

Influence of Rate of Shear on the Viscosity–Concentration Relationship for Dilute Solutions of Cellulose Nitrate. T. E. Timell. *Svensk Papperstidning*, **57**, 844–849 (30 Nov. 1954).

The effect of rate of shear on the viscosity–concentration relationship has been studied for a large number of fractionated and unfractionated cellulose nitrates in ethyl acetate solution. At constant rates of shear and over the concentration range 0·2–1·0 g./litre the reduced viscosity was found to vary linearly with concentration, according to Huggins' equation, but plots of reduced against specific viscosity were non-linear. Martin's equation had a downward curvature, particularly so with the lower velocity gradient. It is concluded that, for the determination of the intrinsic viscosity of cellulose nitrates exhibiting structural viscosity, the reduced viscosities should be recalculated to a constant rate of shear, plotted against concentration, and extrapolated linearly to zero concentration. A non-linear relationship may call for the cubic term in the general viscosity–concentration equation to be included. S. V. S.

Interaction of Benzyl Acetate and Cellobiose α-Octaacetate with Solvents for Cellulose Acetate. W. R. Moore and J. Russell. *J. Appl. Chem.*, **4**, 369–373 (July 1954).

The dielectric-constant method of Giles, Rose, and Vallance (see J.S.D.C., **69**, 101 (1953)) is applied in the study of the interaction of benzyl acetate and cellobiose α-octa-acetate, used as models of cellulose acetate, with solvents for cellulose acetate. In hexane soln. benzyl acetate appears to form complexes with 1 or 1·5 mol. proportions of chloroform and with 2 mol. proportions of *m*-cresol. There is some evidence of the formation of 1 : 1 complexes of cellobiose α-octa-acetate with *m*-cresol and with aniline in dioxan soln., but no evidence is found for complex formation with acetone, ethyl acetate, pyridine, and chloroform. A. E. S.

PATENTS

Coating Paper. Hercules Powder Co. *USP* 2,661,308

A coating adhesive for applying pigments to paper comprises a vinyl copolymer having as one vinyl component a compound containing a masked carboxy group regenerable by hydrolysis, there being enough of it to provide 1 carboxy group to 2–30 mol. of the monomers,

e.g. a methyl methacrylate-vinyl acetate copolymer. High wet-rub resistance is obtained if the coating paper is treated with alum.

USP 2,661,309

A copolymer of $> 50\%$ of a non-acidic compound, e.g. acrylamide and $< 50\%$ of acrylic acid yields a binding agent which gives a coating composition which flows smoothly and evenly to yield a coating of high strength and high wet-rub resistance. C. O. C.

Recording Medium for Stylus Type Oscillographs. Compagnie pour la Fabrication des Compteurs et Materiel d'Usines à Gaz. *USP* 2,662,828

A cellulosic film is coated with extremely fine carbon black suspended in a solvent for the film substance. This results in the surface of the film being dissolved and so in the mixing of part of the carbon black with the upper surface of the film. C. O. C.

Heat-sensitive Copying Paper (IX p. 118).
Transfer Paper (IX p. 118).

XII—LEATHER; FURS; OTHER PROTEIN MATERIALS

Recent Researches in the Chemistry of Leather. A. Kuntzel. *Bull. Assocn. Française Chim. Cuir*, **16**, 111–126 (Aug. 1954).

A review, with three photomicrographs, and 18 references to the literature. J. W. D.

Structure of Collagen. A. A. Tustanovskiĭ, A. L. Zaides, G. V. Orlovskaya, and A. N. Mikhaĭlov. *Doklady Akad. Nauk S.S.S.R.*, **97**, 121–124 (1 July 1954).

Treatment of rat-skin collagen with a citrate buffer of pH 4·0 yields an extract from which the protein "procollagen" [the supposed precursor of collagen (A. A. Tustanovskiĭ, *Biokhimiya*, **12**, 285 (1947))] is precipitated in the form of needle-like crystals and fibres. The residue is freed from any remaining procollagen by treatment with water at 50°C. for 1·5 hr., and the product obtained is given the name "collastromin". Procollagen shows many of the properties regarded as characteristic of collagen—it gives the characteristic staining tests with e.g. silver, picrofuchsine, periodate–fuchsine, and Toluidine Blue; it gives the characteristic X-ray diffraction maxima; and electron-microscopical examination shows that the fibrous form consists of fibrils having the characteristic collagen striations, but varying in diameter according to the method by which the procollagen was isolated from solution. Collastromin, however, consists of non-striated fibrils (diameter 50–70 A.), does not give the characteristic staining tests, and gives only diffuse X-ray diffraction rings, the 2·9-A. and 11-A. maxima characteristic of collagen being absent; it contains protein–polysaccharide complexes. In collagen, the basic supporting structure consists of collastromin fibrils, and these have an oriented, striated covering of procollagen, the composite fibrils being $\sim$ 100 A. in diameter. A. E. S.

Effects of Pressure upon Collagen. A. J. Cruise. *Nature*, **174**, 888–889 (6 Nov. 1954).

When air-dried collagen fibres are subjected to extremely high pressure, liquid globules are exuded. It is suggested that so called dry fibres possess surface films which prevent structural dissociation of the constituent fibrils and ensure the preservation of fibre identity.

J. W. B.

***p*-Nitrophenol as a Fungicide for Leather.** R. M. Lollar and H. K. Steinle. *J. Amer. Leather Chem. Assocn.*, **49**, 605–624 (Sept. 1954).

Leather containing at least 0·2% of *p*-nitrophenol (I) will remain free from mould growth for at least 3 months under tropical conditions, and at least 10 months if stored at 35°C. with almost saturated humidity. The grease in re-tan leather is consumed by moulds, and I thus prevents this loss. Leather will, however, still deteriorate in strength if badly stored under humid conditions, since hydrolytic action occurs and is not, of course, controlled by I. The determination of I in leather (by extraction with $CHCl_3$, and conversion to indophenol blue) has been critically examined, the results are discussed at length, and means of improving the precision of the method are given. There are difficulties in the application of I to leather, and these are discussed. J. W. D.

Differences and Analogies between the Chemical Compositions of Synthetic Tanning Agents and Leather Dyes. L. Loewe. *Österr. Lederztg., Festchrift*, A1–3 (1954): *Chem. Abs.*, **48**, 13249 (10 Nov. 1954).

An attempt to establish the mechanism of the tanning action of dyes with particular reference to their constitution. The connection between formation of hydrogen bonds, dipole and electron structure, and tanning activity of several leather dyes is discussed. C. O. C.

PATENT

Simultaneous Drumming and Vacuum Treatment of Skins—Leather Dyeing. High Vacuum Processes. *USP* 2,662,805

The skins are subjected to high vacuum in the drum and while held under it are treated with unhairing, tanning or dyeing liquors. This greatly speeds up processing, e.g. under a vacuum of 2,000–500 microns Hg the skins are treated with a liquor containing the dye and sulphonated oil for 5 min., air admitted and rotation continued a little longer under atmospheric conditions. Complete penetration of both dye and oil through the leather is obtained, and the dyed leather is fast to rubbing, has good layout and handle, and lies flat without surface wrinkles.

C. O. C.

Water-resistant Protein Materials (VI p. 114).
Effect of Auxiliary and Dressing Agents on the Dyeing of Skins for the Velvet and Glove Trades (VIII p. 117).

XIII—RUBBER; RESINS; PLASTICS

Geometrical Form and Optical Properties of Chain Macromolecules in Solution. V. N. Tsvetkov and É. V. Frisman. *Doklady Akad. Nauk S.S.S.R.*, **97**, 647–650 (1 Aug. 1954).

Mathematical treatment of the relationship between the geometrical form of a macromolecule and the birefringence of streaming solutions of the substance. A. E. S.

Investigation of the Physical Structure of Synthetic Polyamides with the aid of Infrared Absorption Spectra. D. N. Shigorin, N. V. Mikhaĭlov, and S. P. Makar'eva. *Doklady Akad. Nauk S.S.S.R.*, **97**, 711–714 (1 Aug. 1954).

Further experiments (cf. J.S.D.C., **70**, 477 (Oct. 1954)) confirm that the absorption bands given by polyamides at $\sim$ 3300 cm.$^{-1}$ and $\sim$ 3080 cm.$^{-1}$ are to be attributed to the presence of intermolecular hydrogen-bonding of Types I and II (*loc. cit.*) respectively, and indicate that the band at $\sim$ 3210 cm.$^{-1}$ is to be attributed to Type III bonds, which are intramolecular bonds made possible by the folding of the chain (they are found also, in association with a band in the same position, in α-keratin). In conformity with this view, the bands at $\sim$ 3210 cm.$^{-1}$ become very feeble when polyamide fibres (6-, 7-, and 6,6-nylons) are subjected to cold drawing. A. E. S.

Equilibration in Molten Polyamide Mixtures. C. W. Ayers. *J. Appl. Chem.*, **4**, 444–449 (Aug. 1954).

By a partition-chromatography method developed by the author (*Analyst*, **78**, 382 (1953)) it is shown that, when mixtures of 6,6- and 6,10-nylons are heated at 290°C., exchange reactions occur, and a copolymer having a high measure of randomness with respect to the arrangement of the chain units is obtained within 2 hr. A. E. S.

Exchange Reactions between Polyamide Macromolecules. V. V. Korshak and T. M. Frunze. *Doklady Akad. Nauk S.S.S.R.*, **97**, 675–678 (1 Aug. 1954).

The views previously expressed by Korshak (cf. e.g. J.S.D.C., **69**, 227 (1953)) on the exchange reactions occurring in the course of the formation of polyesters and polyamides are further confirmed by experiments on mixed polyamides—When mixtures of polyhexamethylenediamine (polyHMD) azela-ate and polyHMD sebacate, and of polyHMD adipate, polyHMD azela-ate, and polyhexanolactam, are heated, the polycondensates so obtained (which are quite distinct from the homogeneous mixtures obtained immediately after melting the substances together) are identical in properties with those

obtained by heating the corresponding mixtures of monomers (HMD azela-ate + HMD sebacate, HMD adipate + HMD azela-ate + 6-hexanolactam).
A. E. S.

Determination of the Molecular Weight of Polyethylene Terephthalate by End-group Assay. W. Griehl and S. Neue. *Faserforsch. und Textiltech.*, **5**, 423–429 (Oct. 1954).

Mol. wt. of fairly homogeneous polyethylene terephthalate fractions are determined by end-group assay, the hydroxyls being acylated with bromoacetyl bromide and determined as bromine, or converted into urethan groupings with phenyl *iso*cyanate and determined as nitrogen. The results agree closely with viscosimetric values determined in a 1 : 1 mixture of phenol and 1:1:2:2-tetrachloroethane. Tests on unfractionated preparations show that technically valuable polyethylene terephthalates have weight-mean mol. wt. $\overline{M}_w$ (determined viscosimetrically) of 22,000–27,000 and number-mean mol.wt. $\overline{M}_n$ (determined by end-group assay) of 16,000–20,000. The heterogeneity ($\overline{M}_w/\overline{M}_n - 1$) is thus 0·35–0·40, so that the polycondensation reaction cannot proceed by the Flory mechanism, which requires a value of 0·99.
A. E. S.

Effect of Plasticisers on the Mechanical Properties of Polyvinyl Chloride. R. I. Fel'dman. *Doklady Akad. Nauk S.S.S.R.*, **97**, 1033–1036 (21 Aug. 1954).

For plasticised polyvinyl chloride in the elastic state (three main states are recognised— vitreous, elastic, and viscous-flow) the logarithms of the tenacity and of Young's modulus are linear functions of the mole fraction of plasticiser (tricresyl phosphate, dioctyl phthalate, heptyl nonyl phthalate, dibutyl phthalate, dibutyl sebacate, chlorinated diphenyl). General equations for these properties can be written in which the logarithm of the value of the property for the system is expressed as a linear combination of the logarithms of these properties for the separate components (the coefficients being the mole fractions of the components), although for the plasticiser these "properties" may have no physical reality, their values being obtained only by calculation or extrapolation. These equations enable the composition of polymer–plasticiser systems having given properties to be calculated.
A. E. S.

Densities of Polyvinyl Alcohol Film. H. Tadokoro, S. Seki, and I. Nitta. *Bull. Chem. Soc. Japan*, **27**, 451–454 (Oct. 1954).

The densities of polyvinyl alcohol film at moist states have been determined by a flotation method at 25°c. The density–water content curve shows a maximum at ca. 1·5% water content. Pore-size distributions for the film and for regenerated cellulose are calculated from desorption data, and the results discussed and compared with those of other workers for cellulose.
W. R. M.

PATENTS

Metallic Films on Plastic Bases. National Research Development Corpn. *BP* 719,779

The required metallic film is deposited upon a primary base to which it does not permanently adhere. It is then coated with a solution of the plastic base in sufficient thickness to yield a self-supporting film on drying. This thin film is then floated off to yield a thin film of plastic coated with metal. Floating is accomplished by immersing the primary base bearing the metal and plastic films into a liquid such that adherence of the metallic film to the plastic is greater than to the primary base. In many cases floating can be done in water.
C. O. C.

Imparting Anti-static Properties to Vinyl Resins. Dictaphone Corpn. *BP* 720,023

Incorporation of 2–10% of a monoamide of a straight chain hydroxy acid, e.g. *N*-2-hydroxyethyl ricinoleamide, imparts antistatic properties to vinyl polymers and copolymers.
C. O. C.

Rendering Transparent Thermoplastic Resins Flame-resistant. Diamond Alkali Co. *USP* 2,664,411

Incorporation of triphenylstilbene and a chlorinated paraffin wax of on average 18–36 C and 35–75% chemically combined Cl, imparts flame-resistance to transparent thermoplastic resins without impairing their transparency.
C. O. C.

Solvents for Acrylonitrile Polymers (III p. 109).
Relationship of the Properties of a Polyamide to the Structure of its Repeating Unit (VI p. 114).
Dichroic Study on Polyvinyl Alcohol Fibre. IV—Theoretical Relation between Intrinsic Double Refraction and Dichroism (VI p. 114).
Stabilising Polyacrylonitrile to Heat (VI p. 114).
Continuously Embossing Fabrics or Sheets of Synthetic Thermoplastic Material (X p. 119).

XIV—ANALYSIS; TESTING; APPARATUS

Small-scale Filter-paper Chromatography—A Rapid Two-dimensional Procedure. L. B. Rockland and J. C. Underwood. *Anal. Chem.*, **26**, 1557–1563 (Oct. 1954).

A small-scale two-dimensional filter-paper chromatographic procedure has been developed for the separation of amino acids and related cpd. As little as 0·1 µg. of amino acid contained in 0·1–1·0 µl. of soln. can be separated and identified on a 5-in. square filter paper. *tert.*-Butanol–H·COOH–water is used as first solvent, and a single-phase phenol–ammonia–water mixture as the second. Variations in R_f values as a function of irrigation temp. have been studied for both solvents over the range 5–40°c. A chart is reproduced which shows the loci of 60 amino acids, peptides, carbohydrates, and organic acids on a diagrammatic small-scale two-dimensional chromatogram; the R_f values and ninhydrin colours are tabulated. Specimen chromatograms obtained with various hydrolysates are reproduced and discussed.
J. W. D.

Rapid Microtitration of Sulphate. J. S. Fritz and S. S. Yamamura. Sixteenth Midwest Regional Meeting of the American Chemical Society. *Anal. Chem.*, **26**, 1666 (Oct. 1954).

Small concn. of SO_4^{2-} can be determined by a direct titration with 0·01 M-$Ba(ClO_4)_2$ using Thorin (1-*o*-arsenophenylazo-3:6-disulphonic acid) as indicator. The titration is carried out in 70–90% alcohol, in the apparent pH range 3·5–4·0. The end-point is sharp, and equilibrium is rapidly attained. Cations are best removed by means of an ion-exchange column, before the soln. is titrated. Phosphate interferes, and may be removed by rapid pptn. with $MgCO_3$. An accuracy within ±1 p.p.m. is attainable with concn. of SO_4^{2-} as low as 10 p.p.m.; an error of $\not>$ 1% is associated with higher concn.
J. W. D.

Analysis of Synthetic Anionic Detergent Compositions. R. House and J. L. Darragh. *Anal. Chem.*, **26**, 1492–1497 (Sept. 1954).

Available methods for determining alkylbenzenesulphonates and alkyl sulphates are briefly reviewed, and several modifications are detailed, whereby the method due to Epton (*Trans. Faraday Soc.*, **44**, 226 (1948)) may be improved in accuracy and ease of conduct. A procedure is given for the preparation of the pure sulphonic acid used in standardising the quaternary cpd., and the recommended overall method of analysis is given in full. Alkylarylsulphonates and alkyl sulphates may be determined in presence of one another by applying the above titrimetric procedure before and after hydrolysis of the sample soln. with 0·5 N-H_2SO_4 to destroy the alkyl sulphate. Low-mol.wt. sulphonates, added to modify the properties of the detergent, may be separated by virtue of the fact that alkylbenzenesulphonates (Alk of $\not>$ 4C) are much more sol. in aq. acid than in wet acidified ethyl ether; the identification and the estimation of such components by means of their ultraviolet spectra are discussed, and three spectra are reproduced. The determination of inorg. SO_4^{2-} by a modification of the method

of Ogg, Willits, and Cooper (*Anal. Chem.*, **20**, 83 (1948)) is described and discussed. Methods for the determination of water, oil, polyphosphates, silicates, carbonates, borates, and additives such as foam promoters are mentioned; references to the literature are given. Colour may be measured by tristimulus colorimetry. For soln. colours, the amount of colour is expressed on a linear scale in terms of equivalent colour bodies, permitting direct linear comparison of samples, and more quant. analysis of the causes of colour formation. This is discussed at length. J. W. D.

Polarographic Determination of Dissolved Oxygen in Dilute Sulphite Waste Liquor. H. S. Levine and O. J. Williams. *Anal. Chem.*, **26**, 1297–1302 (Aug. 1954).

The method, by which dissolved oxygen may be accurately determined in water containing up to 3% of sulphite waste, is given in full detail. J. W. D.

Determination of Ammonium in Ammonium Bisulphite Spent Liquor. O. Samuelson and N.-H. Schöön. *Svensk Papperstidning*, **57**, 850–852 (30 Nov. 1954).

The possibility of determining ammonium in ammonium bisulphite spent liquor by distillation with excess sodium hydroxide has been investigated. Owing to a reaction between ammonia and the organic matter in sulphite spent liquor, ammonia cannot be completely recovered. By very rapid steam distillation this loss is reduced to 0·3–0·4%. An ion-exchange method for the determination of free nitrogen has also been worked out. S. V. S.

Determination of Pyridinium Nitrogen. F. E. Crane and R. M. Fuoss. *Anal. Chem.*, **26**, 1651–1652 (Oct. 1954).

Pyridinium salts are decomp. with Na_2O_2, and this liberates ca. 75% of the nitrogen in directly titratable form; the mixture is steam-distilled into an Erlenmeyer flask. The residual soln. is acidified and concentrated, and subjected to Kjeldahl digestion, whilst the first steam distillate is also concentrated. Finally, the remaining, digested soln. is steam-distilled to augment the first distillate, and the combined soln. is titrated in the usual way. Experimental details are given, and the results of proving analyses are cited and discussed. J. W. D.

Titrimetric Determination of Sulphates by Diazo Titration of Benzidine Sulphate. R. E. Keller and R. H. Munch. *Anal. Chem.*, **26**, 1518–1519 (Sept. 1954).

Sulphate is determined, in sulphonates, by pptn. of benzidine sulphate from an alcohol-water soln., re-solution of the ppt. in 6 N-HCl, and potentiometric titration with KNO_2 (0·1 M.) in presence of KBr, using a Pt–W electrode system. The max. error for the 0–2% sulphate range is ±3%, and for the 2–12% range it is ±0·8%, of the amount added. In the analysis of samples containing 50 mg. of SO_4^{2-}, up to 5 mg. of PO_4^{3-} (as Na_2HPO_4), 10 mg. of CrO_4^{2-} (as K_2CrO_4), 500 mg. of Cl^- (as NaCl), and 10 mg. of $FeCl_3$ may be present without causing interference; if these amounts are exceeded, the ions must be either removed or complexed. The procedure is fully described. J. W. D.

Identification of Di- and Poly-amines and Amino-hydroxy Compounds as Fission Products of Azo Dyes. [Constitution of Commercial Azo Dyes.] E. D. G. Frahm. *Rec. Trav. chim.*, **73**, 748–758 (Sept.–Oct. 1954).

Di- and poly-amines, as well as aminohydroxy cpd. in dil. soln. resulting from the hydrosulphite reduction of azo dyes, can be isolated and identified by benzoylation of such soln., either immediately or after separation of one or more of the other fission products. Single amines are obtained in a high degree of purity, but when mixtures of amines result, separation is necessary; this presents no difficulty if the component amines differ in their solubility in acid and/or alkaline media, but if fractional crystallisation is required, difficulties may arise. Benzoylation is quant. if properly conducted. The fission products of ca. 100 dyes, belonging mainly to the Chlorantine Fast and the Coprantine ranges, are indicated, and the m.p. of several benzoyl cpd. not previously mentioned in the literature are listed; these are all amido or diamido derivatives of subst. simple aromatic nuclei. The constitutions of five different dyes (covered by 17 commercial names), established in the course of the work, are given. Experimental details are given in full. J. W. D.

Analysis of Hair Dyes and Rinses. S. H. Newburger. *J. Assocn. Off. Agric. Chem.*, **37**, 793–796 (1954): *Chem. Abs.*, **48**, 12377 (25 Oct. 1954).

In the analysis of hair dyes containing a mixture of *p*-aminophenol and 2:5-diaminotoluene or *p*-phenylenediamine, the diacetyl derivative of the diamine is separated from that of the phenol, and each compound is determined individually by ultraviolet spectrophotometry. C.O. C.

Analysis of Mascaras, Eyebrow Pencils, and Eye Shadows. P. W. Jewel. *J. Assocn. Off. Agric. Chem.*, **37**, 796–798 (1954): *Chem. Abs.*, **48**, 12377 (25 Oct. 1954).

Dissolve 2 g. of molten sample in 5 ml. of a straight-cut aliphatic solvent of boiling range 75–100°c., boil for 5 min., add 35 ml. of additional solvent, bring to the boil, and centrifuge immediately. Decant, repeat extraction until pigment residue loses no further weight, dry at 100°c., and weigh. C. O. C.

National Printing Ink Research Institute Standard Method for Tinting Strength of Printing Ink Pigments. W. C. Walker. *Amer. Ink Maker*, **32**, (2), 25–27, 63 (1954): *Chem. Abs.*, **48**, 13236 (10 Nov. 1954).

Details are given of comparative testing procedure. C. O. C.

Cystine Analysis of Wool—Methods and Applications. H. Zahn and K. Traumann. *Melliand Textilber.*, **35**, 1069–1073 (Oct. 1954).

Details are given of the colorimetric estimation of cystine with tungstophosphoric acid. Changes during slaughtering, liming, scouring, and chlorinating were followed by this method, which was used also for estimating the wool content of wool–Perlon, wool–Redon, and wool–casein mixtures. S. R. C.

New Solvent System for Separation of Amino Acids by Paper Chromatography. R. A. Clayton and F. M. Strong. *Anal. Chem.*, **26**, 1362–1363 (Aug. 1954).

Ninhydrin-positive compounds are resolved satisfactorily by means of a mixture of methyl ethyl ketone, propionic acid, and water (75 : 25 : 30). The solvents are completely miscible, and the composition of the system is thus unaffected by temp. variation. The movement of 24 amino acids has been studied: the R_f differences amongst the individual amino acids are as great as those reported with any existing unidirectional systems. The method, which is fully described, gives consistent and reproducible results under given experimental conditions, and it may also be used two-dimensionally. The observed R_f values for 24 amino acids are tabulated. J. W. D.

Small-scale Filter-paper Chromatography—Factors affecting the Separation and the Sequence of Amino Acids. J. C. Underwood and L. B. Rockland. *Anal. Chem.*, **26**, 1553–1557 (Oct. 1954).

Studies are reported in the determination of the relationships between solvent character, water content of the solvent, acidic and basic solvent supplements, filter papers, and the separation and sequences of the amino acids on small-scale filter-paper chromatograms. With few exceptions, the sequence of the amino acids within the acidic, basic, neutral, and cyclic groups was found to be independent of the 9 solvents and 3 filter papers examined. Considered as independent groups, the sequences of the 4 amino acid groups are influenced to the greatest degree by the acidity or basicity of the solvent. Solvents supplemented with acidic or basic materials, such as H·COOH or ammonia, tend to improve the separation and reproducibility in all cases, especially with acidic and basic types. The most satisfactory separations of individual amino acids are obtained with *tert.*-butyl alcohol–water–formic acid and phenol–water–ammonia. All

experimental details are given, the results are tabulated, two chromatograms are reproduced, and there are two photographs illustrating the techniques involved.
J. W. D.

Influence of Chemical Treatment on the Properties of Wool. I—Alkali Solubility as a Measure of Sulphuric Acid Degradation. J. H. Dusenbury, E. H. Mercer, and J. H. Wakelin. *Text. Research J.*, **24**, 890–899 (Oct. 1954).

The effects of acid damage on several single-fibre properties and on the resistance of fabrics to flex abrasion have been measured for correlation with alkali-solubility data. The view that the cortex of the wool fibre consists of a resistant fraction, the paracortex, and a less resistant fraction, the orthocortex, is used to explain the mechanism of the alkali-solubility test on acid-damaged wool. Wool treated with formaldehyde exhibits greatly decreased alkali solubility, but fails to show a corresponding improvement in physical properties, and possible reasons for this are discussed.
A. B.

Determination of Carboxyl End-groups in a Polyester, Polyethylene Terephthalate. H. A. Pohl. *Anal. Chem.*, **26**, 1614–1616 (Oct. 1954).

In this semimicro procedure, the polyester is dissolved rapidly in benzyl alcohol at 203°c., then the soln. is quickly mixed with $CHCl_3$, and the polyester is titrated with NaOH (0·1 N. in benzyl alcohol), with phenol red as indicator. It is imperative that the polymer should be dissolved as quickly as possible, and a correction is made for the decomp. which occurs during the soln. process. The method is described in detail, and there is a diagram of a new and simple type of automatic pipette which was used in the work.
J. W. D.

Determination of Abrasion Resistance. H. Sulser. *Textil-Rund.*, **9**, 285–307 (June); 348–354 (July); 399–409 (Aug.); 468–480 (Sept.); 514–526 (Oct.); 569–581 (Nov. 1954).

A comprehensive paper, beginning with a general discussion of testing serviceability, methods of determining abrasion resistance (A), and the evaluation of the results of such tests. A table gives details of 34 machines for measuring A, but only four were used in the experimental work reported. This showed that different methods or different abrading elements give results in qualitative, though not in quantitative, agreement. Emery paper, etc. is quite useless, and metal is unsuitable. The type of abrading element used must be appropriate for the type of wear expected, but, in general, bristles are preferred. The use of harder or softer abrading brushes and the pressure applied have little effect on results, but changes in R.H. affect both the material to be tested and the brushes. Removal of dust and the tension of the sample have little influence. Alterations in the brushes through use are considerable and are caused by changes in the bristle-ends and also in R.H. due to the heat developed. To compensate for these changes it is best to compare directly the A of samples with that of a reference material. Comparison of worn and artificially abraded samples, both macro- and micro-scopically, and the consistently low A found for defective fabrics illustrate the success of these methods of testing. The most suitable methods of testing the A of 14 types of material are listed. Measurement of the work of abrasion was unpromising. For a worsted uniform cloth good correlations exist between A and wt./sq. metre and extension at break, but none between A and breaking strength. 74 references.
H. E. N.

Temperature of Contraction of Fibres as an Aid to Identification—Apparatus. J. N. Banks and E. R. Johnston; J. M. Preston and A. S. Brown. *J. Textile Inst.*, **45**, T 941–T 943 (Dec. 1954).

A simple melting-point apparatus comprises a copper block ($3\frac{1}{4} \times 1\frac{1}{4} \times 1\frac{1}{4}$ in.) hollowed to fit closely over a $3 \times \frac{1}{2}$ in. 75-w. tubular heater element. At one end of the block is a pocket for a thermometer bulb, and the fibres are mounted in a recess which accommodates an overlying glass slide. The temperature "gradient" along the block is < 1°c., and accurate melting points of thermoplastic fibres can be rapidly obtained.

In a reply (J.M.P. and A.S.B.) it is pointed out that, although the apparatus is capable of high accuracy, a great variation in melting point can be brought about by altering other conditions: rapid heating and the presence of air can give values for 6,6-nylon 10–20°c. below that obtained in absence of air in a determination lasting 24 hr. For this reason it is much more informative to quote a melting range.
J. W. B.

Quantitative Analysis of Silk-Cellulosic Fibre Mixtures. C. Earland and D. J. Raven. *J. Textile Inst.*, **45**, T 943–T 944 (Dec. 1954).

A reagent prepared by dissolving 10 g. of fused $CaCl_2$ in 100 ml. of 90% (wt./wt.) formic acid dissolves silk rapidly in the cold without affecting cotton or viscose rayon. Suggested conditions are 50 ml. of reagent per gram of mixture for 20 min. at 110°c. Residual cellulose is collected on a coarse sintered glass filter, washed twice with 10-ml. portions of reagent, and washed thoroughly with cold water. No correction is necessary for cotton; viscose rayon gives values 0·7% high. The reagent is considered to be much more convenient than other silk solvents such as ammoniacal nickel hydroxide, phosphoric acid, and dichloroacetic acid.
J. W. B.

Artificial Surface Dirts for Detergency Studies with Painted Surfaces. W. E. Shelberg, J. L. Mackin, and R. K. Fuller. *Ind. Eng. Chem.*, **46**, 2572–2579 (Dec. 1954).

The preparation of artificial soils of controlled particle size distribution, similar in composition to natural urban and shipboard dirt, is described, together with an apparatus for converting them into aerosols which are allowed to settle on to the test panels of painted metal or other hard surface material. Detergency is then assessed on the basis of percentage soil removal by weighing the soiled panels before and after a standardised washing treatment.
W. K. R.

Studies in Detergency. X—Electron Microscopy. E. Götte, W. Kling, and H. Mahl. *Melliand Textilber.*, **35**, 1252–1257 (Nov. 1954).

Cleansing can be observed as a reduction in the number of particles, e.g. of iron oxide and natural soil on cotton, visible under the electron microscope when the number or duration of washings is increased. Increasing fineness of the soil particles renders washing more difficult, especially below 0·2 μ. When no further particles are visible under the electron microscope, the fibres are macroscopically clean.
S. R. C.

Tinctorial Strength, Depth (or Apparent Strength) of Dyeings, and "Money Value" of Dyes. I. H. Godlove. *Amer. Dyestuff Rep.*, **43**, P 685–P 690, P 696 (11 Oct. 1954).

A simple empirical formula, based on the concept that apparent strength, or depth, of dyeing is measured by departure from white in a properly constructed visual colour solid similar to (but not identical with) the Munsell colour solid, has been developed for calculating the apparent strengths from Munsell notations. It has been used with fair success for two years and has been applied to a number of dyes of several classes, for which the average relation between ratio of depths and ratio of concentrations has been found. When slight shading is necessary in bulk dyeing, the correct direction of shading can be predicted.
J. W. B.

Selection of Colour Matchers. V. G. Jolly. *J. Oil & Col. Chem. Assocn.*, **37**, 666–669 (Dec. 1954).

Colour aptitude, although it is a faculty which may be fostered and developed, must be inborn; it cannot be inculcated. About 8% of men and 0·8% of women are colour defectives, and these should first be eliminated in the selection of colour matchers. In the present state of knowledge of colour vision, the best preliminary tests appear to be the Ishihara and the Anomaloscope. The general test developed by the National Institute of Industrial Psychology (W. O'D. Pierce, "The Selection of Colour Workers" (1934)) appears to have been unsatisfactory, and the method has not found general acceptance. The Farnsworth-Munsell Test for Colour Discrimination, in which 85 graded plastics discs, forming collectively a colour circle, are placed in order under defined conditions, is quite satisfactory in that it is not costly, is easy to administer, gives an immediate index to an individual's colour aptitude, and detects and defines defective colour vision (if this has not been discovered by other means). The overall scores obtained by colour defectives are frequently better than those returned by people with

normal colour vision, since they may register low scores only in the confusion regions. A colour aptitude test devised by the Inter-Society Colour Council Committee (of America) and now sponsored by the Federation of Paint and Varnish Production Clubs, if applied to candidates who have passed the Ishihara and Anomaloscope tests, appears to be a valuable aid to the selection of employees who are likely to profit by training, and to become good colour matchers. The test consists in the matching of 48 coloured chips, arranged as 4 finely graduated series of 12, with a similar set, taken one at a time from a special dispenser to which each chip must be returned before going on to the next. The colours chosen are approx. to Munsell hues: 7·5 RP (red–purple), 7·5 YR (yellow–red), 2·5 PB (purple–blue), and 5·0 BG (blue–green), at a brightness of ca. Munsell 5/ value. Graduation is in terms of saturation, ranging from /3 to /6. Each of the 4 series of chips is in random order, and the correct matching of any one chip from the dispenser is very exacting. Lighting and viewing conditions are specified, and ca. 1½ hr. is required to complete one test. A time limit may be imposed, but if this is done the chips should be maintained in a constant random order, so that comparisons between different subjects are fully significant. The scores obtained may be correlated with a classification based on known degrees of practical skill. The max. is virtually unattainable, and a wide spread of scores facilitates the grading of subjects, only ~ 5% of whom reach the "excellent" class. Better scores are obtained with increasing practice and skill in colour matching, but the limit still varies widely from one operator to another. J. W. D.

Colour Space for Colour Grading Purposes. G. W. Ingle. *A.S.T.M. Bulletin*, (201), 36–40 (Oct. 1954).

The yellowness of transparent materials may be graded by means of a technique, consisting in the application of a simplified equation for colour difference derived from that of MacAdam. J. W. D.

Light Fastness and Phototropy. H. Zukriegel. *Melliand Textilber.*, **35**, 1074–1075 (Oct. 1954).

The Heliotest instrument (*ibid.*, **33**, 44 (1952)) showed that the illumination of dyed fibres in sunlight resulted in crystal lattice changes which recovered in diffuse daylight. The rate of recovery was reduced with an increasing number of sunlight exposures. This phototropy is a function of the light fastness of the dye. S. R. C.

Notes on the E.C.E. Standard Methods for Determining the Colour Fastness of Textiles. P. Rabe. *Textil-Praxis*, **9**, 1052–1058 (Nov. 1954).

Observations on the tests, with special reference to alkali, scrooping, kier-boiling, ironing, chlorine, decatising, carbonising, and light fastness. S. R. C.

Textile-shrinkage Control Processes and Test Methods. J. F. Warner. *Amer. Dyestuff Rep.*, **43**, P 726–P 729 (25 Oct. 1954).

The phenomenon of fabric shrinkage is discussed particularly with regard to woven cotton fabrics, compressive shrinkage, resin stabilisation, and AATCC test methods. J. W. B.

Study of Factors influencing the Quantitative Determination of Methylpentoses and Ketohexoses with Anthrone. J. R. Helbert and K. D. Brown. Sixteenth Midwest Regional Meeting of the American Chemical Society. *Anal. Chem.*, **26**, 1667 (Oct. 1954).

Most prior methods for estimating carbohydrates by the anthrone method have tacitly assumed 100°c. to be optimum for developing the anthrone–carbohydrate colour. The following optimum temp. and times are indicated by a study of the intensive and extensive aspects of heating—

	°c.	Min.
Glucose ...	90	16
Galactose ...	90	8
Arabinose ...	80	4
Rhamnose ...	70	13
Fucose ...	70	13
Fructose ...	60	7
Sorbose ...	60	8

J. W. D.

Quantitative Determination of Sugars on Paper Chromatograms by a Reflectance Method. R. M. McCready and E. A. McComb. *Anal. Chem.*, **26**, 1645–1647 (Oct. 1954).

Direct reflection density measurements at 515 mμ. on paper chromatograms of the coloured spots developed from reducing sugars and aniline–trichloroacetic acid, or fructose and derivatives with phosphoric acid–resorcinol, have been found to be reproducible, and to follow a linear relationship between the log. of the sugar concn. and the reflection density. The concn. of one or more pentoses in a mixture containing a uronic acid may be determined. All details are given. J. W. D.

Determination of Uronic Acid in Alduronic Acids, Polysaccharides, and Oxycelluloses. A. Mellor. *Svensk Papperstidning*, **57**, 741–744 (31 Oct. 1954).

The quantitative determination is based on an evaluation of kinetic data obtained by measuring the rate of evolution of CO_2 from essentially homogeneous H_2SO_4 solutions of the materials. Uronic acid carboxyl contents may be determined with an accuracy of ±4%. S. V. S.

Properties of Periodate-oxidised Polysaccharides. III—Estimation of α-Glycol Groupings in a Polysaccharide. V. C. Barry, J. E. McCormick, and P. W. D. Mitchell. *J.C.S.*, 3692–3696 (Nov. 1954).

It is shown that the N and S contents of the polymers obtained by the condensation of periodate-oxidised polysaccharides with *iso*nicotinhydrazide and thiosemicarbazide give a measure of the proportion of sugar units vulnerable to periodate oxidation in the polysaccharides. H. H. H.

Properties of Periodate-oxidised Polysaccharides. IV—Products obtained on Reaction with Phenylhydrazine. *J.C.S.*, 4020–4023 (Nov. 1954).

Periodate-oxidised polysaccharides condense with phenylhydrazine to give amorphous products. When heated with phenylhydrazine in acetic acid, the oxypolysaccharides and their phenylhydrazine deriv. give mixtures of osazones, which are chromatographically separated on alumina. H. H. H.

Specific Test for Formaldehyde in Air. W. E. MacDonald. *Amer. Ind. Hyg. Assocn. Quart.*, **15**, 216–219 (1954): *Chem. Abs.*, **48**, 13535 (25 Nov. 1954).

Collect a sample of the air in a fritted-glass bubbler containing water, transfer a 4·0-ml. aliquot to a 30-ml. flask, add 0·1 ml. of 1% chromotropic acid, mix, add 6 ml. conc. H_2SO_4, mix, cool to room temp., and compare the colour visually with standards prepared in the range 1–20 μg. HCHO. As little as 0·1 μg. HCHO per ml. of sample can be detected. C. O. C.

PATENT

Measuring the Surface Areas of Pigments. American Cyanamid Co. *BP* 717,966

Pigments having surface areas > 0·5 sq.m./g. have their surface area measured by placing a weighed sample in an evacuated chamber. Gas at constant rate of flow is then allowed to enter the chamber, the sample in which has been cooled to approximately the b.p. of the gas. The time is measured for the gas in the chamber to reach a pressure relative to saturation pressure of 0·1–0·3, preferably 0·2 and from this calculating the surface area of the sample, e.g. by using the Brunauer, Emmett, and Teller equation. C. O. C.

Fluidity and Critical Pigment Volume of Industrial Paint Materials (V p. 113).
Amino Acids in Animal Fibres and Superpolyamides (VI p. 114).
Influence of Rate of Shear on the Viscosity-Concentration Relationship for Dilute Solutions of Cellulose Nitrate (XI p. 119).
p-Nitrophenol as a Fungicide for Leather (XII p. 120).

XV—MISCELLANEOUS

Plasticised Sulphur Compositions for Traffic Marking. C. K. Hancock. *Ind. Eng. Chem.*, **46**, 2431–2435 (Nov. 1954).

Molten sulphur (at not > 160°c.) containing 5–15% Thiokol A (polyethylene tetrasulphide), 1–3% Hansa Yellow type of pigment, 2% wood rosin, and 0·5% bactericide provides a yellow marking composition which gives good performance on both concrete and asphalt surfaces. The setting time in min. is roughly equivalent to the percentage of Thiokol. W. K. R.

THE SOCIETY OF DYERS AND COLOURISTS
LONDON SECTION

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The Third London Lecture

will be given at the

WALDORF HOTEL ALDWYCH LONDON WC

on Friday 4th March 1955 at 7 pm

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Deputy Keeper of the Records, Corporation of London

Subject "The Guilds of the City of London"

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SITUATIONS VACANT AND WANTED *etc*

Replies may be addressed "Box —, Society of Dyers and Colourists," Dean House, 19 Piccadilly, Bradford 1, Yorks., where all communications relating to these Advertisements, which are treated in strict confidence, should be addressed.

The Publications Committee is prepared to receive Advertisements relating to Situations Vacant, Situations Wanted, or Miscellaneous Items for insertion on this page of the Journal. Advertisements of Situations Wanted are gratis to individual members, but must not exceed twenty-four words in length.

All inquiries relating to Advertisements in the Journal should be addressed to The General Secretary, The Society of Dyers and Colourists, Dean House, 19 Piccadilly, Bradford 1, Yorks.

SITUATIONS VACANT

The engagement of persons answering these advertisements must be made through a Local Office of the Ministry of Labour or a Scheduled Employment Agency if the applicant is a man aged 18–64 inclusive or a woman aged 18–59 inclusive unless he or she, or the employment, is excepted from the provisions of the Notification of Vacancies Order 1952.

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JOHN WALTON OF GLOSSOP LTD. (a subsidiary of Tootal Ltd.) have a vacancy for a Printing Colourist. This is a new post in a developing unit which offers a wide opportunity to a first-class man. Applications should be addressed to the Secretary, Longdendale Works, Hollingworth, Manchester.

LABORATORY ASSISTANTS REQUIRED for colour application research laboratory, preferably with previous experience. Box V62

TEXTILE CHEMIST required by the Co-operative Wholesale Society Limited, in the Technical Research Department. Technologist to be of graduate standard and experienced in natural and synthetic fibres and textile analysis. Send full details of qualifications and experience and salary to — Co-operative Wholesale Society Limited, Central Labour Department, 1 Balloon Street, Manchester 4, endorsed "Chemist, Technical Research Department".

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THE British Leather Manufacturers' Research Association invites applications from science graduates with experience of research on dyeing or dyestuffs and with a knowledge of the technology of dyeing either leather or textiles. There are two vacancies, one in the Scientific Officer grade £450 × 25 to £600; the other in the Principal Scientific Officer grade £1000 × 50 to £1350; starting salaries dependent on age, qualifications and experience. Benefits under F.S.S.U. Applications should be addressed to The Director of Research, B.L.M.R.A., Milton Park, Egham, Surrey.

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A.T.I. Aged 35. Returning to England in April after 9 years experience with vertical concern in India. F.T.C. City and Guilds Dyeing of Wool and Cotton. Seeks executive position, Works or Production Manager in Dyeing and Finishing Plant. Box W533

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THE Society has several requests for back numbers of the *Journal* but the following issues are out of stock. If any member wishes to dispose of any of these copies, the Society will re-purchase them at 2s. per copy. January 1939 to December 1944; February to March 1945; January to March, and June 1946; January to June 1952; January and July 1954. Replies to be addressed to the General Secretary, Society of Dyers and Colourists, Dean House, 19 Piccadilly, Bradford.

WANTED. Proceedings of a symposium on Fibrous Proteins held at The University, Leeds, on 23rd, 24th and 25th May 1946. Replies to be addressed to the General Secretary, The Society of Dyers and Colourists, Dean House, 19 Piccadilly, Bradford.

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Yeadon, E., formerly of 18 Benton Park Crescent, Rawdon, Leeds

Young, L. A., formerly of 51 St. Michael's Lane, Headingley, Leeds 6

The Society of Dyers and Colourists

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on

1st April 1955

at the

Queens Hotel Leeds

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Advance ticket reservations are invited by letter addressed to the Society.

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